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ANOMALOUS MECHANICAL BEHAVIOR OF HIGH-DENSITY NANOCRYSTALLINE GOLD

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High-density nanocrystalline (n-) Au with more than 99 % of the theoretical density is prepared by applying the gas deposition method and its mechanical property is investigated by the tensile test. The yield stress of the high-density n-Au at the strain rate of about 10^{-3} s^{-1} exceeds 600 MPa at 100 K and decreases to about 200 MPa at room temperature. The yield stress decreases with decreasing strain rate or with increasing temperature, e.g., 160 MPa at 4.5 x 10^{-5} s^{-1} at room temperature and 140 MPa at 10^{-3} s^{-1} at 348 K. Under a static stress of about 100 MPa, n-Au starts a plastic deformation at room temperature but not at 80 K. In contrast, the Vicker's hardness of n-Au is about 5 times higher than that of the bulk Au and increases with decreasing mean grain size. These observations suggest that the diffusion and slip processes at grain boundaries govern the mechanical behavior of n-Au.
Key words : nanocrystalline, gold, high-density, mechanical property, grain boundary.

1. INTRODUCTION

Ultra-fine polycrystals with the mean grain size (d) less than several tens nm are called as nanocrystalline (n-) materials and expected to possess unusual properties owing to both the small crystallite size and the much increased volume fraction of grain boundaries (GBs) /1/. The mechanical behavior is one of the most principal properties and it becomes very important for the technological use of the materials. From the characteristic structure of n-materials, it is expected that the phenomena relevant to the GBs such as the superplasticity are much enhanced compared with the conventional polycrystalline (poly-) materials with d of ~ μm, and many investigations have been reported /2/.

From the early stage of the investigation, it has been reported that the strength of n-metals is much higher than that of poly-metals, where the increasing manner of the strength with decreasing d can be described by the Hall-Petch rule, i.e., the strength increases with $d^{-1/2}$. However, without the further work, it is premature to conclude that the deformation process in n-metals is controlled by the dislocation. In contrast to the high strength, the early works reported the very low modulus in the n-metals /3,4/. However, recent works report that the modulus in the high-density n-metals is very similar to that of the poly-metals /5,6/. Further, it is claimed that the n-metals containing a considerable amount of pores show the lower modulus than poly-metal ones /6/, and that the modulus in GBs of n-metals is nearly equal to that in the perfect crystalline. In our previous study, the Young's modulus in the high-density n-Au prepared by the gas deposition method showed a rapid decrease with increasing temperature above 200 K, suggesting that some thermally activated motions come in at GBs /7/. In that case, it is expected that the plastic deformation in n-Au depends on the strain rate as well as temperature. To clarify this issue, we have investigated the temperature dependence of plastic behavior in the high-density n-Au prepared by the gas deposition method.

2. EXPERIMENTAL PROCEDURE

High-density n-Au specimens were prepared by applying the gas deposition method /8/. Ultra-fine Au particles produced by the inert-gas condensation technique were accelerated by utilizing a gas jet flow and directly deposited on the glass substrate at room temperature /9/. A computer controlled XY-stage was used to draw several n-Au line patterns of 0.8 mm width, 20mm length and 20μm thickness on the substrate. Then the n-Au specimens were removed from the glass substrate by using a thin razor. The density of the ribbon specimens was determined by the Archimedes' method and d was evaluated from the Scherrer's analysis of the X-ray diffraction peaks. It is noted that d estimated from the X-ray diffraction peak analysis showed good agreement with d measured in the STM surface image.

The tensile test of the ribbon specimens was carried out by using the Instron type tensile machine (Shimazu Auto-graph AGS-G) /9/. For the tight clamping, both edges of a specimen were rapped by Au foils of 0.1 mm thickness and then clamped by an Al holder. The Al holder with the n-Au specimen was attached on the apparatus as a whole. The strain was monitored from the displacement of the cross head and the stress, by using the load cell, respectively. In order to minimize an effect of thermal expansion, fused quartz pipes were used as the supporting rods and pulling rod. The proper stress-strain curve of the specimen was determined after the subtraction of the

stress-strain curve of the testing apparatus, which was separately measured. For the verification of this procedure, a fused quartz fiber with a cross section of 6.22 x 10^{-9} m^2 was tested, where the Young's modulus of 73.6 +- 0.6 GPa found shows good agreement with 73 GPa in the literature. The strain rate used for the tensile test was 2 x 10^{-3} to 5 x 10^{-5} s^{-1}. The creep tests were also performed to investigate the quasi-static deformation behavior and the Vickers microhardness tests with a load of 0.098 N for 10 s to study the rapid deformation behavior, respectively.

3. RESULTS AND DISSCUSSION

The density of the n-Au ribbon specimens was found in the range between 19.3 and 19.7 g/cm^3 with the experimental accuracy of 0.6 g/cm^3, where no obvious d dependence was found in the d range from 20 to 60 nm. For the calibration, the density of a poly-Au foil was found to be 19.5 g/cm^3. Within the present experimental accuracy, both the density found in the n-Au specimens and in the poly-Au foil show good agreement with the density reported for the bulk Au of 19.32 g/cm^3.

Figure 1 shows the effect of heat-up on d and the Vickers microhardness (H_V) found in the present high-density n-Au specimens, where d starts to increase during heat-up to 400 K accompanied by a large decrease in H_V. An increase in d even at room temperature was also reported in the high-density n-Pd /10/ and n-Cu /11/ prepared by the compaction of ultra-fine particles produced by the inert-gas condensation. That is, the grain growth at moderate temperatures reflects the intrinsic nature of the high-density n-metals. In contrast to the high-density n-metals, the strong retardation of the grain growth up to 1000 K was reported for the low-density n-Au prepared by the gas deposition method /12/. Based on the low Young's modulus about 70 % of the poly-Au value, it is claimed that the n-Au specimens used in /12/ contain pores with the volume fraction of about 26 % /13/.

The plasticity of the high-density n-Au specimens considerably varies with d, strain rate and temperature. At the first, we shall mention the results of the hardness test, which reflects the rapid deformation behavior. Figure 2 shows the dependence of H_V on d, where the value of H_V increases from 0.5 to 2 GPa with decreasing d. The observed dependence of H_V on d appears to be explained by the Hall-Petch rule, i.e., $H_V \sim d^{-1/2}$. The Hall-Petch rule observed for poly-metals with d of ~ μm is attributed to the pile-up mechanism of dislocations at GBs. For n-Pd prepared by the compaction method /14/, the high-resolution electron microscopy indicates the existence of dislocations in the grains. However, for the present n-Au specimens, the preliminary electron microscope observation suggested no dislocations in the grains. Further, no dislocation pinning phenomena were observed for the present n-Au specimens after low-temperature irradiation /15/. On the other hand, it should be mentioned that the Griffis theory for the fracture can explain the $d^{-1/2}$ dependence of the strength if the hardness is governed by the slip deformation between adjacent grains by the stress concentration at the GB interfaces.

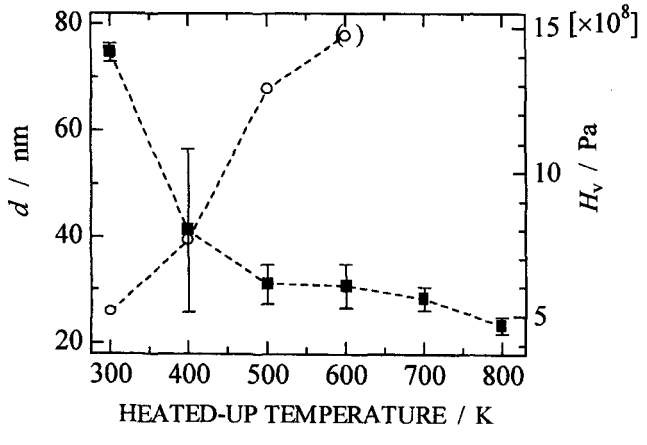

Figure 1. Changes in the mean grain size (d) and the Vickers microhardness (H_V) after heating-up at 20 K/min. d was estimated from X-ray diffraction peak broadening.

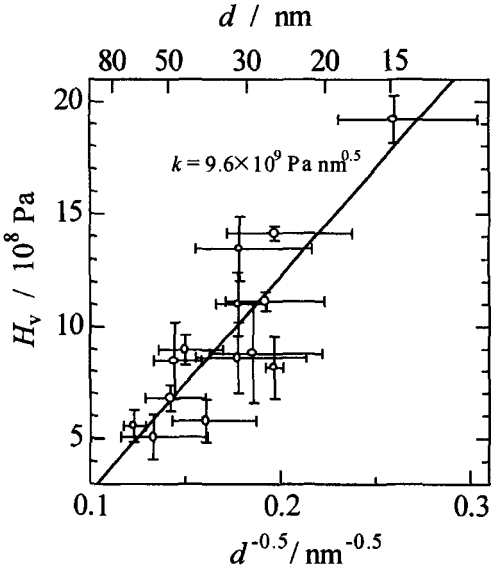

Figure 2. The dependence of the Vickers microhardness (H_V) on d observed for the high-density n-Au at room temperature, where the change in H_V is depicted against $d^{-1/2}$.

Compared with the hardness test, the tensile test would measure the mechanical response at the moderate strain rate. Figure 3 shows the stress-strain curves obtained in the tensile tests of the high-density n-Au specimens with d of 30 nm at the strain rate of 4.5 x 10^{-5} s^{-1} at different temperatures (the nonlinear response seen in the lowest strain range, e.g., below $5x10^{-4}$, may be artificial and a hysteresis at around the maximum strain region is due to the backlash of the apparatus). As seen in Fig.3, the yield stress of n-Au increases with decreasing temperature.

Figure 4 shows the dependence of the yield stress on the strain rate which was observed for the n-Au specimen with d of 30 nm, where we define the yield stress as the stress where the strain deviates by 0.01 % from the linear relationship. At 298 K, the yield stress shows a rapid increase with increasing the strain rate below 10^{-3} s^{-1} and a moderate increase above that. The dependence of the yield stress on the strain rate found at 348 K is similar to that observed at 298 K except that the values of the yield stress found at 348 K are considerably lower than those at 298 K. In contrast, even for the quasi-static tests at 100 K, a n-Au specimen shows no yielding up to the stress of about 600 MPa and then a sudden fracture of the specimen takes place /16/. These observations indicate that the plastic deformation process in the high-density n-Au specimens varies with temperature. We have reported that the Young's modulus of the high-density n-Au showed a deviatory decrease from that of poly-Au above 200 K /7/. That is, the Young's modulus of the high-density n-Au is more than 95 % of the poly-Au value at 80 K and 90 % at room temperature. These results suggest that a certain thermal activation process in GBs is responsible for the both the anelastic and the plastic deformation behaviors above 200 K, and a nearly athermal plastic deformation process governs the plastic behavior below 200 K. In the case of the heterogeneous plastic deformation in amorphous alloys at low temperatures, it is known that the yield stress becomes to be about one third of the hardness /17/. If we could apply this relationship to n-Au, the hardness about 1.8 GPa is expected at 80 K. Unfortunately, we have not measured the temperature dependence in the hardness. However, it is noted that this expected value is almost same to H_V observed for the specimen with d of 15 nm at room temperature. In the amorphous alloys, the formation and propagation of the local slip between atoms (shear band) is proposed for the heterogeneous deformation process /17/. We tentatively surmise that the anomalous mechanical behavior of n-Au reflect the competition between the fast and slow deformation processes. The slower deformation is governed by probable diffusion at GBs. The faster one may be govern by the corrective slip between the grains along GB interfaces. To confirm these issues, the further study is now in progress.

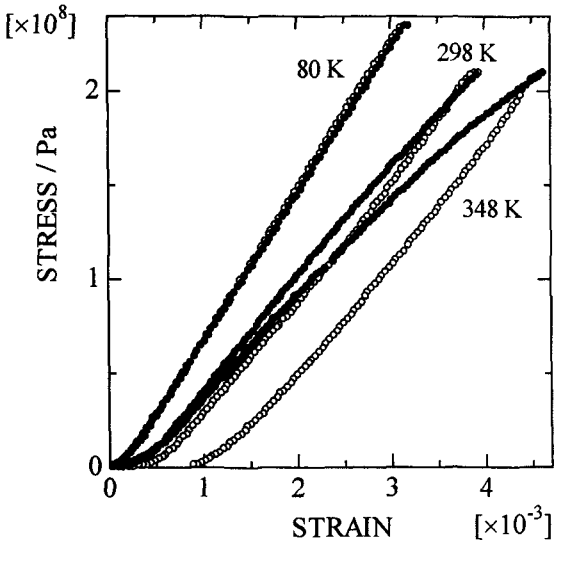

Figure 3. Stress-strain curves observed in the tensile test of the high-density n-Au with the strain rate of 4.5 x 10^{-5} s^{-1} at different temperatures. Filled symbols indicate the data observed during loading and open ones, those during unloading.

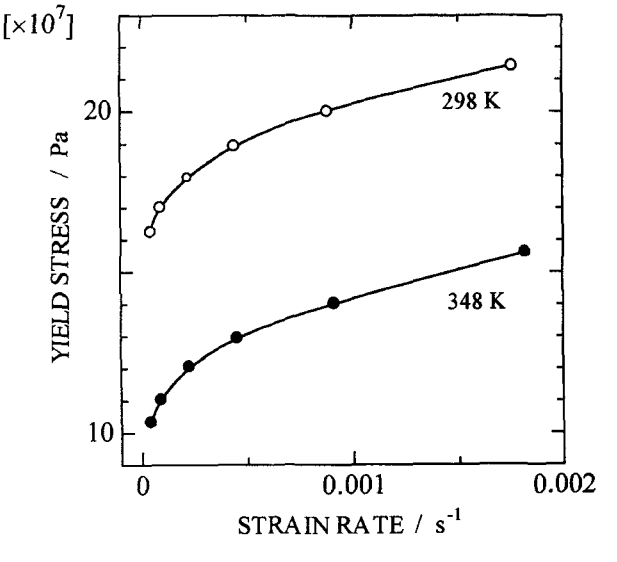

Figure 4. Changes in the yield stress of the high-density n-Au with the strain rate and temperature. The yield stress is defined at the stress where 0.01 % plastic strain is attained.

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