Characterization and Determination of Elastic Property of High-Density Nanocrystalline Gold Prepared by Gas-Deposition Method

Tanimoto Hisanori, Sakai Seiji, Kita Eiji, Mizubayashi Hiroshi

Materials Transactions
Volume 44
Issue 1
Pages 94-103
Year 2003

(C)2003 The Japan Institute of Metals

URL: http://hdl.handle.net/2241/101579
doi: 10.2320/matertrans.44.94

<table>
<thead>
<tr>
<th>著者</th>
<th>Tanimoto Hisanori, Sakai Seiji, Kita Eiji, Mizubayashi Hiroshi</th>
</tr>
</thead>
<tbody>
<tr>
<td>営業</td>
<td>材料力学学会誌</td>
</tr>
<tr>
<td>版</td>
<td>&quot;Materials Transactions&quot;</td>
</tr>
<tr>
<td>年</td>
<td>2003</td>
</tr>
<tr>
<td>セクション</td>
<td>44</td>
</tr>
<tr>
<td>号</td>
<td>1</td>
</tr>
<tr>
<td>厳計</td>
<td>94-103</td>
</tr>
</tbody>
</table>

doi: 10.2320/matertrans.44.94
Characterization and Determination of Elastic Property of High-Density Nanocrystalline Gold Prepared by Gas-Deposition Method

Hisanori Tanimoto\textsuperscript{1}, Seiji Sakai\textsuperscript{1,*}, Eiji Kita\textsuperscript{2} and Hiroshi Mizubayashi\textsuperscript{1}

\textsuperscript{1}Institute of Materials Science, University of Tsukuba, Tsukuba, 305-8573, Japan
\textsuperscript{2}Institute of Applied Physics and Center for Tsukuba Advanced Research Alliance (TARA), University of Tsukuba, Tsukuba, 305-8573, Japan

Nanocrystalline (n-) Au specimens with the density of 19400±200kg/m\(^3\) were prepared by the gas deposition method. Since rearrangement of n-Au particles on the specimen surfaces takes place just after landing, the grain boundary energy of (0.3±0.15)J/m\(^2\) is comparable with 0.45 J/m\(^2\) reported for the bulk polycrystalline (p-) Au, and the concentration of vacancy type defects is about 15×10\(^{-17}\) m\(^{-3}\) in the as deposited state decreasing with the grain growth. The Young modulus observed at 10 K is almost the same to that estimated under the condition that stresses applied to the constituent crystallites are equal among all the crystallites while strains are variable.

(Received September 27, 2002; Accepted November 18, 2002)

Keywords: nanocrystalline gold, grain boundary energy, Young modulus, vacancy concentration, gas deposition method

1. Introduction

Nanocrystalline (n-) metals\textsuperscript{1,2} are considered as composite materials composed of nanocrystallites and the grain boundary (GB) regions, where new properties such as superior magnetism\textsuperscript{3} and super-plasticity\textsuperscript{4} have been reported. The characteristic properties of n-metals such as the grain growth temperature, the excess vacancy type defects and the elastic response are disputed. The grain growth in n-Au specimens containing considerable pores is reported to be strongly retarded.\textsuperscript{4} On the other hand, it is indicated that the grain growth in the high-density n-Pd\textsuperscript{5} and n-Au\textsuperscript{6} specimens starts slightly above room temperature. For n-Fe specimens, the size-dependent grain growth is reported.\textsuperscript{7} Theoretically, it is suggested that the grain growth process in n-metals would be retarded in comparison with that in the bulk polycrystalline (p-) metals when the excess vacancy type defects contained in the GB regions should move into the constituent crystallites.\textsuperscript{8,9} The excess vacancy type defects may play an important role on the thermal stability of the high-density n-metal, as well as the grain growth process.

The very low elastic modulus reported in the pioneer works\textsuperscript{10–12} of n-metals is probably due to pores contained in the n-metal specimens. Recently, Sanders et al.\textsuperscript{13–15} studied on n-Cu and n-Pd specimens with the relative density, ρ/ρ\textsubscript{0} (ρ\textsubscript{0}: the full density), of 82–98%, and reported that the Young modulus extrapolated to the full density state shows good agreement with the bulk value. Qin et al.\textsuperscript{16} reported that in n-Ag specimens with ρ/ρ\textsubscript{0} of 90–98%, the Young modulus extrapolated to the full density state is lower by about 15% than the bulk value. In our previous work\textsuperscript{17} on n-Au specimens with ρ/ρ\textsubscript{0} > 98%, the Young modulus is about 90% of the bulk value. Ultrasonic wave velocity measurements on high-density n-Fe and n-Ti specimens also show that the elastic moduli are about 95% of the bulk values.\textsuperscript{18} That is, the values of the Young modulus observed for the high-density n-metals is comparable to the intrinsic bulk values. On the other hand, the theoretical value of the Young modulus of a polycrystalline material is known to be in between ϵ\textsubscript{0}E\textsubscript{0} and ϵ\textsubscript{f}E\textsubscript{0}, where ϵ\textsubscript{0}E\textsubscript{0} denotes the Young modulus estimated under the condition that stresses applied to the constituent crystallites are equal among all the crystallites while strains are variable, and ϵ\textsubscript{f}E\textsubscript{0} denotes the Young modulus estimated under the opposite condition. ϵ\textsubscript{0}E\textsubscript{0} and ϵ\textsubscript{f}E\textsubscript{0} are given by the following eqs. (1) and (2),

\[ \epsilon_0 E_0 = \sum_{(hkl)} (R_{(hkl)}/E_{(hkl)}), \]  
\[ \epsilon_f E_0 = \sum_{(hkl)} (R_{(hkl)}/E_{(hkl)}), \]

where R\textsubscript{(hkl)} and E\textsubscript{(hkl)} denote the fractional volume and the Young modulus of the constituent (hkl) crystallites, and Young modulus of the GB region is assumed to be the bulk value. The mean value between ϵ\textsubscript{0}E\textsubscript{0} and ϵ\textsubscript{f}E\textsubscript{0} is called as the Young modulus under the Hill’s assumption, \( \text{Hill} E_0 \). It is noted that ϵ\textsubscript{0}E\textsubscript{0} < ϵ\textsubscript{f}E\textsubscript{0} is expected for a metal with the anisotropic Young modulus, and the Young modulus of Au strongly depends on the crystallographic direction.\textsuperscript{19} Then, one may expect that the Young modulus of n-Au specimens can be compared with ϵ\textsubscript{0}E\textsubscript{0} and ϵ\textsubscript{f}E\textsubscript{0} giving an insight into the deformation mode in n-metals. In the present work, we evaluated the Young modulus of the high-density n-Au specimens and discussed in a view point of deformation mode.

2. Experimental Procedures

High-density n-Au specimens were prepared by the gas deposition (GD) method.\textsuperscript{20,21} The GD apparatus was composed of an evaporation chamber, a deposition chamber and a helium circulation system with purification columns,\textsuperscript{17} where the two chambers were connected by a narrow pipe (the transfer pipe, hereafter). Prior to deposition, the apparatus was evacuated down to 10\(^{-4}\) Pa for one day to
minimize outgassing from the inner walls. During the deposition, the helium gas circulation system was in operation, where the evaporation and deposition chambers were evacuated by rotary vacuum pumps and a He gas was simultaneously supplied to the evaporation chamber at the rate of 35 L/min. The He gas pressure in the evaporation chamber was maintained at 66.7 kPa, and that in the deposition chamber at 133 Pa. The monitored purity of He gas was better than 99.9999% during the deposition, because pure He gas is necessary for obtaining contamination-free and pore-free n-Au specimens. In the evaporation chamber, 99.99% pure Au in a graphite crucible was heated by an RF-induction heater, where n-Au particles were formed by the inert-gas condensation process just above the Au melt. Then, n-Au particles were suctioned by the transfer pipe and immediately transferred onto a glass substrate in the deposition chamber by a He gas jet flow in the transfer pipe. In the previous works, an agglomeration of n-Au particles took place in the transfer pipe with a tapered-off nozzle. Here, we used a straight transfer pipe in order to avoid the undesirable agglomeration.

A model calculation for helium gas flow in the present straight transfer pipe with 1.8 mm inner diameter showed that the flow speed at the inlet and outlet was about 200 and 350 m/s, respectively, where an adiabatic compressible flow in the straight pipe at Fanning friction factor of 0.004 is assumed. In the present experiment, a mass fraction of Au particles against the helium gas flow was less than 10⁻³. In this case, Au particles with diameter less than several tens nm are accelerated to a speed of the helium gas flow in a few μs, and are transferred onto a substrate in a few ms. In the present experiment, the deposition rate of the n-Au particles was controlled by the Au melt temperature, T_L. Figure 1(a) shows T_L as a function of the RF-induction power, P_i, where T_L was measured by the pyrometer. Since T_L increases from 1670 to 1850 K with increasing P_i from 3.6 to 4.8 kW, the deposition rate of n-Au particles can be denoted by P_i instead of T_L.

In order to avoid a grain growth during the deposition, the temperature of the glass substrate was kept below about 270 K using a cold stage. Ribbon shape n-Au specimens 0.02–0.1 mm thick, 1 mm wide and 23 mm long were prepared by controlling the position of the glass substrate. The specimen face of 1 mm wide and 23 mm long will be referred to as the specimen flat-surface, hereafter. To detach the n-Au specimen from the glass substrate, a water drop was given on one edge of the specimen and the edge corner was gently scratched with a thin razor blade. Then, the n-Au specimen spontaneously peeled off from the glass substrate. The n-Au specimens were prepared by the GD method, where the evaporation and deposition chambers were sectioned face.

A preliminary positron lifetime study was conducted for the n-Au specimens in the as-prepared state. The lifetime spectra could be explained by two constituents with the lifetimes of τ_p1 and τ_p2. The value of about 185 ps for τ_p1 is similar to the positron lifetime in single vacancies. The value of about 350 ps for τ_p2 corresponds to the positron lifetime in micro aggregates of a few vacancies. The long lifetime component associated with pores was not detected. The intensity ratio, I_p1/I_p2, of the τ_p1 component to the τ_p2 component was about 9/1, indicating that most of the vacancy-type defects contained in the present n-Au specimens are of a single vacancy type. Ito et al. reported the positron lifetime spectra with similar τ_p1 and τ_p2 for n-Au specimens prepared by the GD method, however, the value reported for I_p1/I_p2 is about 3/2 which is much smaller than 9/1 found for the present n-Au specimens. For the positron
lifetime spectra reported for various n-metal specimens prepared by the gas-condensation and compaction method, $I_{P1}/I_{P2}$ is less than 3/2, and $I_{P2}$ is as large as micro voids containing 10 to 15 vacancies.\textsuperscript{26,27}

The X-ray diffraction (XRD) measurements were made by using the Cu $K_{\alpha}$ radiation (40 kV, 30 mA), where the instrumental line broadening was corrected by using the spectra of Si powders. The XRD measurement in the $\theta$–$2\theta$ scan mode was conducted with two different geometrical setups, i.e., the XRD scattering ($q_\perp$) vector was normal to or parallel to the specimen flat-surface (the $q_\perp$ or $q_1$ conditions, hereafter). The XRD spectra measured under the $q_\perp$ and $q_\parallel$ conditions will be referred to as $I_\perp$ and $I_\parallel$, and the ($hkl$) reflection peak in $I_\perp$ as $I_{\perp(hkl)}$, respectively. The crystallites whose ($hkl$) direction is normal (or parallel) to the specimen flat-surface are referred to as the ($hkl$)$_\perp$ (or ($hkl$)$_\parallel$) crystallites, hereafter.

The annealing of the n-Au specimens was performed in a vacuum of $10^{-4}$ Pa for 1.8 ks. In order to avoid undesirable constraint during annealing, a ribbon of the n-Au specimen was sandwiched by two glass plates which were separated by a gap slightly larger than the specimen thickness. A change in the specimen length, $\Delta L/L_0$, due to annealing was measured as follows. Two small markers with a gage length, $L$, of about 20 mm were indented on the specimen flat-surface by the Vickers hardness tester, and a change in $L$ due to annealing was measured at RT by using an optical microscope. The Vickers hardness, $H_v$, was measured under the loading of 0.098 N for 5 s at RT. The tensile tests were carried out using an Instron-type tensile apparatus in the temperature range between 80 K and 300 K. The vibrating reed measurements with a strain amplitude of about $10^{-4}$ were carried out at the resonant frequency of about 300 Hz in the temperature range between 10 K and 300 K. (See the previous work\textsuperscript{17} for the apparatuses.)

3. Results

3.1 Characterization of n-Au specimens in the as-prepared state

As mentioned, the deposition rate of ultrafine Au particles on a substrate was controlled by adjusting $P_i$. Figure 1(b) shows the deposition rate as a function of $P_i$. Figure 1(c) is the redrawing of Fig. 1(b), but here the deposition rate is plotted against the vapor pressure of Au which is estimated from the $T_L$ vs. $P_i$ data shown in Fig. 1(a) and the thermodynamic data.\textsuperscript{28} The deposition rate of ultrafine Au particles is increased linearly with the vapor pressure of Au in the present experimental condition. We shall refer to $P_i$ instead of the deposition rate below. In Fig. 1(b), the classification of the n-Au specimens by the deposition rate is indicated, i.e., the type-L specimens prepared at $P_i$ below 4 kW and the type-H specimens at $P_i$ above 4 kW, respectively.

In Fig. 2(a), the density of the n-Au specimens in the as-prepared state is plotted as a function of $P_i$. Figure 2(b) shows the density measured for the n-Au specimens annealed at 1100 K for 1.8 ks and for that of a 5N p-Au foil with the similar size as a reference. All the values observed for the type-L specimens, the type-H specimens and the p-Au foil show good agreement with 19.32 g/cm$^3$ reported for the bulk Au value in literature.\textsuperscript{28} The densities measured for the n-Au specimens are listed in Table 1.

Figures 3(a) and (b) show examples of the XRD spectra $I_\perp$ and $I_\parallel$ observed for the type-L specimens. $I_{\perp(111)}$ is strong, $I_{\perp(220)}$ moderate and $I_{\perp(222)}$, $I_{\perp(311)}$ and $I_{\perp(331)}$ much weaker, while $I_{\parallel(111)}$, $I_{\parallel(200)}$, $I_{\parallel(220)}$, $I_{\parallel(311)}$ and $I_{\parallel(222)}$ reflections are consistent with those of a bulk powder specimen. It is not shown here but $I_\perp$ and $I_\parallel$ observed for the type-H specimens are similar to those observed for the type-L specimens except that the relative strengths for $I_{\parallel(hkl)}$ are different between the type-L and type-H specimens. Figure 4 shows the volume fraction of the ($hkl$)$_\parallel$ crystallites, $R_{\parallel(hkl)}$, found for the n-Au specimens as a function of $P_i$, where $R_{\parallel(hkl)}$ for the predominant $I_{\parallel(200)}$, $I_{\parallel(220)}$ and $I_{\parallel(111)}$ reflections are plotted. $R_{\parallel(hkl)}$ is estimated using the following equation,

$$R_{\parallel(hkl)} = \left( A_{\parallel(hkl)}/F^2L^2 \right) \sum_{(mno)} \left( A_{\parallel(hkl)}/F^2L^2 \right).$$

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Density ($\text{kg/m}^3$)</th>
<th>$d_{\text{STM}}$ (nm)</th>
<th>$d_{\text{STM}(111)}$ (nm)</th>
<th>$d_{\text{STM}(hkl)}$ (nm)</th>
<th>$3(\Delta L/L_0) - (\Delta a/\alpha_0)_{100,K}^b$</th>
<th>$T_{\text{GO}}^c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type-L</td>
<td>19400 ± 200</td>
<td>~20</td>
<td>~40</td>
<td>60–80</td>
<td>~15 × 10$^{-4}$</td>
<td>400–500</td>
</tr>
<tr>
<td>Type-H</td>
<td>19400 ± 200</td>
<td>~20</td>
<td>~40</td>
<td>—</td>
<td>—</td>
<td>300–400</td>
</tr>
</tbody>
</table>

$^a$Mean grain size estimated from STM surface morphology, $d_{\text{STM}}$ obtained from the $I_{\perp(111)}$ reflection and the modified Williamson–Hall plot, respectively (see text).

$^b$Concentration of the vacancy type defects found after annealing at 400 K.

$^c$Onset temperature of grain growth for annealing time of 1.8 ks.
where $A_i^{[hk]l}$ denotes the integrated intensity of $I_i^{[hk]l}$, $F$ is the structure factor, and $L^*$ is the Lorenz polarization factor. The results in Fig. 4 indicate that the values of $R_i^{[hk]}$ are different between the type-L and the type-H specimens, but remain constant among the each type.

The mean grain size in the n-Au specimens was estimated from the STM surface morphology and the peak broadening of the XRD reflections. Figure 5 shows an example of the STM images observed for the specimen flat-surface of the type-L specimens, where the sizes of dome-like swells are between 15 and 30 nm. The secondary agglomerates which were observed in the previous work, pores and cracks are not found in the present specimens. STM images very similar to Fig. 5 were observed for the sectional surface of the type-L specimens, and also for the specimen flat-surface and the sectional surface of the type-H specimens. Figure 6(a) shows an example for the $q_\perp$ dependence of the line width, $\Delta q_\perp$, of the $I_i^{[hk]l}$ reflections observed for the type-L specimens. As seen in Fig. 6(a), the $\Delta q_\perp$ vs. $q_\perp$ data cannot be explained by a linear relationship (the Williamson-Hall analysis), indicating that the mean grain size and/or internal strain are considerably different among the various $[hk]l$ crystallites.

Figure 6(b) is a redrawing of Fig. 6(a), but here the modified Williamson-Hall analysis is applied to the data, where $C$ is a contrast factor reflecting the strain anisotropy. The $\Delta q_\perp$ vs. $q_\perp C^{0.5}$ plot shown in Fig. 6(b) can be explained assuming that the mean grain size is similar among the various $[hk]l$ crystallites, and falls between 60 and 80 nm which is about three times larger than that found in the STM images. On the other hand, as shown in Fig. 3, the fractional volumes of the $(100)_{\perp}$, $(110)_{\perp}$, $(311)_{\perp}$ and $(331)_{\perp}$ crystallites are much smaller than that of the $(111)_{\perp}$ crystallites, indicating that the $(100)_{\perp}$, $(110)_{\perp}$, $(311)_{\perp}$ and $(331)_{\perp}$ crystallites are embedded in the matrix of the $(111)_{\perp}$ crystallites. In such a case, the mean grain size for the $(100)_{\perp}$, $(110)_{\perp}$, $(311)_{\perp}$ and $(331)_{\perp}$ crystallites are not the same as the $(111)_{\perp}$ crystallites. It is noted that the application of the Scherrer’s equation gives about 40 nm for the mean grain sizes of the $(111)_{\perp}$ crystallites and about 20 nm for the $(100)_{\perp}$ crystallites, respectively (see Fig. 9), which show good agreement with the grain sizes found in the STM images. Figure 7 is the $q_\perp$ dependence of $\Delta q_\perp$ observed for the type-H specimens. The $\Delta q_\perp$ vs. $q_\perp$ data observed for the type-H specimens cannot be explained by the modified Williamson-Hall analysis with a single parameter (not shown here). The result shown in Fig. 7 suggests that in the type-H specimens, a distribution of internal strains and/or the mean grain size is considerably different among the various $[hk]l$ crystallites. Applying the Scherrer’s equation to the data shown in Fig. 7, we find that the mean grain sizes of the $(111)_{\perp}$ and the $(100)_{\perp}$ crystallites are about 40 nm and the internal strains may be different between these crystallites. It is noted that the mean grain sizes found in Fig. 7 show good agreement with the grain sizes found in the STM images.
sizes found in the STM images. In the present study, the mean grain sizes were determined for the predominant (111)\textsubscript{h} crystallites by using the Scherrer’s equation. The grain sizes estimated from the STM images and the XRD spectra are listed in Table 1.

We shall discuss a process for branching off of the specimens briefly. As shown in Fig. 3, the (111)\textsubscript{h} crystal is predominant among various (hkl)\textsubscript{h} crystallites for both the type-L and type-H specimens, indicating that ultrafine Au particles undergo a certain rearrangement on the specimen flat surface just after landing. On the other hand, the $R_i$ data shown in Fig. 4 suggest that the degree of rearrangement is not the same between the type-L and type-H specimens, where the rearrangement may not be completed for the type-H specimens because of the higher deposition rates.

Referring to the deposition rate shown in Fig. 1(b), the lower bound of the deposition rate for the type-H specimens is about 800 nm/s, which corresponds to the top on top stacking rate of about 76 particle/s or the arrival time interval of about 0.013 s when the dense packing of the ultrafine Au particles with 20 nm diameter is assumed. The detailed process of the relaxation is out of the present scope.

Figures 8(a) and (b) show examples of the changes in the relative intensities of $I_{i(hkl)}$ by annealing observed for the type-L and the type-H specimens, respectively. The annealing was carried out at the desired temperature, $T_{ann}$, for 1.8 ks. For the type-L specimens, $I_{i(111)}$ is predominant even after annealing at 1100 K (the data for $T_{ann} > 700$ K are not shown).
here). In contrast, a strong increase in \( I_{L(200)} \) and a complimentary decrease in \( I_{L(111)} \) were observed for the type-H specimens after annealing. Figures 9(a), (b) and (c) show changes in the grain size \( d_{L(440)} \) and the Vicker’s hardness, \( H_v \), as a function of \( T_{\text{ann}} \), where \( d_{L(440)} \) is estimated from the \( I_{L(440)} \) reflection by applying the Scherrer’s equation. It is noted that \( H_v \) of the n-Au specimens decreases with increasing the mean grain size in the present range.17) As seen in Figs. 9(a) to (c), the onset temperature of grain growth, \( T_{\text{GG}} \), is in the range between 400 and 500 K for the type-L specimens and between 300 and 400 K for the type-H specimens, respectively. The values of \( T_{\text{GG}} \) observed for the type-L and type-H specimens are listed in Table 1.

We carried out differential scanning calorimetry (DSC) measurements of the n-Au specimens, where a continuous energy release was observed during warm-up from 350 to 750 K. A total energy release between 350 and 750 K was \((5 \pm 2) \times 10^5 \text{J/mol} \) for both the type-H and type-L specimens. As seen in Fig. 9, the grain growth proceeds between 350 K and 700 K. The assumption that the energy release of \((5 \pm 2) \times 10^5 \text{J/mol} \) reflects the reduction of the GB regions gives the GB energy of \((0.3 \pm 0.15) \text{J/m}^2 \) for the n-Au specimens with the grain size of 20 nm, which is comparable with 0.45 J/m\(^2\) reported for the bulk Au at RT.31) It is noted that for n-Ni prepared by the electrodeposition method, the energy release of 415.7 J/mol was observed at around 606 K and attributed to the reduction of the GB regions by the grain growth.32)

3.2 Mechanical responses of the n-Au specimens

Figures 10(a) and (b) show examples of the stress-strain curve observed for the type-L and type-H specimens at the strain rate of \(4.5 \times 10^{-3} \text{s}^{-1} \), respectively. The loading and unloading processes were successively made in the elastic region at temperatures between 80 to 300 K. For both the type-L and type-H specimens, the stress-strain curve observed at 77 K showed the linear elasticity and that at RT revealed a hysteresis between the loading and unloading runs which showed a complete recovery after a prolonged elapsed time. In the present tensile tests, the Young modulus was evaluated from the linear part in the stress-strain curve observed during loading. The Young modulus of the n-Au specimens was also evaluated by means of the vibrating reed method at the resonant frequency of ~300 Hz in the temperature range between 10 and 300 K. Figure 11 shows the Young modulus as a function of temperature observed for
the type-L and the type-H specimens, where both the data from the tensile test in the strain range of $10^{-3}$ and from the vibrating reed measurements in the strain range of $10^{-6}$ are depicted. It is noted that in Fig. 11, the data from the vibrating reed measurements are calibrated to the mean value of the data from the tensile tests at 80 K, where the amount of calibration is smaller than the experimental error. The temperature dependence of the Young modulus of both the type-L and type-H specimens is similar to that reported for the poly-Au below 200 K. As shown in Fig. 11, the Young modulus of both the type-L and type-H specimens shows a decrease from the parallelism with that of the poly-Au above 200 K, where the decrease is larger for the tensile test data than for the vibrating reed measurement data. That is, the anelastic strain revealed above 200 K, $\varepsilon_{\text{an},>200\text{K}}$, is composed of $\varepsilon_{\text{an},>200\text{K}-\text{I}}$ and $\varepsilon_{\text{an},>200\text{K}-\text{II}}$, where $\varepsilon_{\text{an},>200\text{K}-\text{I}}$ is the linear anelastic strain responsible for the decrease in the Young modulus observed with a strain amplitude of $10^{-6}$ and $\varepsilon_{\text{an},>200\text{K}-\text{II}}$ is revealed for the applied stress beyond a few MPa with the distributed relaxation times (see Fig. 10 and Ref. 6).

Figures 12(a) and (b) show changes in the internal friction of the type-L and type-H specimens after annealing, where the strain amplitude used is $10^{-6}$. The relaxation peak at around 95 K (the 95 K $Q^{-1}$-peak) and the rapid increase above 200 K ($Q^{-1}_{>200\text{K}}$) are observed in the as-deposited state. The 95 K $Q^{-1}$-peak and $Q^{-1}_{>200\text{K}}$ diminish after annealing at 500 K, where the grain growth is strongly progressed (see Fig. 9). These features indicate that both the 95 K $Q^{-1}$-peak and $Q^{-1}_{>200\text{K}}$ are associated with anelastic processes in the GB regions. We surmise that $\varepsilon_{\text{an},>200\text{K}-\text{I}}$ is associated with $Q^{-1}_{>200\text{K}}$. Further, $\varepsilon_{\text{an},>200\text{K}-\text{II}}$ is also associated with a certain anelastic process in the GB regions because it can be observed in n-Au specimens but not in poly-Au specimens. A certain characteristic process associated with several atoms in the GB of the n-metals appears to be responsible for $\varepsilon_{\text{an},>200\text{K}}$, however, the detailed mechanisms are not known at the present.

4. Discussion

4.1 Vacancy type defect in high-density n-Au

It is known that, when Schottky-type defects are introduced in materials, the specific volume shows a slight increase. Simmons and Ballufi\textsuperscript{34} carried out the simultaneous measurements of the fractional changes in the lattice parameter, $\Delta a/a_0$, and the specimen length, $\Delta L/L_0$, during heating, and succeeded to evaluate the equilibrium concentration of thermal vacancies, $C_v^{(eq)}$, as a function of the specimen temperature as,

$$C_v^{(eq)} = 3(\Delta L/L_0 - \Delta a/a_0)^{C_v^{(eq)}}. \tag{4}$$

As already mentioned, the preliminary positron study suggests that the present n-Au specimens in the as-prepared state contain the vacancy type defects whose concentration, $C_v$, may be comparable with $C_v^{(eq)}$ near the melting temperature. If it is the case, $C_v$ should decrease after annealing. Experimentally, one can expect a parallel change between $\Delta L/L_0$ and $\Delta a/a_0$ for annealing out of internal...
stresses, and an opposite change between $\Delta L/L_0$ and $\Delta a/a_0$ for a variation in $C_v$. Then, $C_v$ can be estimated from the simultaneous measurements of $\Delta L/L_0$ and $\Delta a/a_0$ at a given temperature after annealing by using the following equation,

$$C_v = 3(\Delta L/L_0 - \Delta a/a_0).$$  \hfill (5)

Figures 13(a) and (b) show $\Delta a/a_0$ and $\Delta L/L_0$ observed at RT for the type-L and the type-H specimens as a function of $T_{\text{ann}}$, respectively, where $a_0$ is the bulk lattice constant and $L_0$ is the length found after annealing at 1100 K. In order to improve the accuracy, $a$ is determined by applying Nelson-Riley’s function \(^{35}\) to the $I_1$ data. Figure 13(c) shows a change in $3(\Delta L/L_0 - \Delta a/a_0)$ found for two type-L specimens and one type-H specimen. For both the type-L and type-H specimens, $3(\Delta L/L_0 - \Delta a/a_0)$ shows an increase for $T_{\text{ann}}$ and then a decrease for $T_{\text{ann}}$ between 400 and 700 K. We surmise that the increase found between 300 and 400 K is associated with an increase of vacancy type defects due to a relaxation of internal strains, and that the decrease observed between 400 and 700 K is associated with annealing out of vacancy type defects by the grain growth. The increase in $3(\Delta L/L_0 - \Delta a/a_0)$ at $T_{\text{ann}}$ between 300 and 400 K is compatible with the view that the excess vacancy type defects are associated with the structural relaxation before the grain growth.\(^{8,9}\) It is noted that for n-Cu prepared by the electodeposition method, a small energy release of 3.2 J/nmol was observed at around 423 K and supposed to reflect a recovery of the stored strains.\(^{36}\) Then, we estimate $C_v$ in the n-Au specimens after annealing at 400 K as about $15 \times 10^{-4}$, assuming that an atomic volume of the vacancy type defect is the same to that of a lattice vacancy. It is noted that $C_v$ of $15 \times 10^{-4}$ is the same order of the thermal vacancy concentration in bulk Au just below $T_m$. For n-Ni specimens prepared by sputtering, Liu et al.\(^{37}\) observed a significant increase in $a$ by $20 \times 10^{-4}$ in $(\Delta a/a)$ after annealing and considered that annealing out of vacancy type defects was responsible for it. The increase in $(\Delta a/a_0)$ observed in the present n-Au specimens by annealing is about $5 \times 10^{-4}$, suggesting that $C_v$ in the present n-Au specimens is lower than that in the n-Ni specimens prepared by sputtering.

The Vicker’s Hardness data shown in Fig. 9(c) indicate that the grain growth of the n-Au specimens strongly progresses between 350 K and 500 K and gradually at elevated temperatures. Except for the increase in $3(\Delta L/L_0 - \Delta a/a_0)$ at $T_{\text{ann}}$ between 300 and 400 K, the decrease in $C_v$ by annealing appears to be parallel to the increase in the grain size. This parallelism suggests that most of vacancy-type defects are in the GB regions. The retardation of the grain growth was reported for n-Fe specimens prepared by ball-milling,\(^{71}\) and we observed the retarded grain growth for the n-Au films prepared by sputtering method.\(^{38}\) We surmise that the grain growth of n-metals are governed by the properties of the GB regions.

### 4.2 Young modulus and deformation mode of high-density n-Au

In Fig. 11, the Young modulus at 10 K, $E_{\text{obs,10K}}$, is found to be 83 ± 1.5 GPa for the type-L specimen and 78 ± 1.5 GPa for the type-H specimens, respectively, and these values are compiled in Table 2. Firstly, an effect of the lattice dilatation on the Young modulus is taken into account. From the Mössbauer spectroscopy of n-Fe particles,\(^{39}\) it is reported that a decrease in the Debye temperature and an increase in the lattice constant from the bulk values are found with decreasing the size. From the computer simulation for the structural and elastic properties of Cu–Ni thin multilayers,\(^{40}\) the increase in the Young modulus with decreasing the lattice constant is reported. The fractional change in the Young modulus, $(\Delta E/E_0)_{\text{dila}}$, due to the lattice dilatation, $(\Delta a/a_0)_{\text{dila}}$, can be estimated as $(\Delta E/E_0)_{\text{dila}} = -16(\Delta a/a_0)_{\text{dila}}$ for n-Fe particles\(^{39}\) and $(\Delta E/E_0)_{\text{dila}} = -14(\Delta a/a_0)_{\text{dila}}$ for Cu–Ni thin multilayers\(^{40}\), at $(\Delta a/a_0)_{\text{dila}} \ll 1$. Then, we assume the relationship of $(\Delta E/E_0)_{\text{dila}} = -15(\Delta a/a_0)_{\text{dila}}$ for the n-Au specimens. As seen in Fig. 13(a), $(\Delta a/a_0)$ in the as-deposited state is negative. By substituting $(\Delta a/a_0)_{\text{dila}}$ in the as deposited state to the relationship of $(\Delta E/E_0)_{\text{dila}} = -15(\Delta a/a_0)_{\text{dila}}$, one can find $(\Delta E/E_0)_{\text{dila}} = +4 \times 10^{-3}$ and $+7 \times 10^{-3}$ for the type-L and the type-H specimens, respectively. The proper Young modulus free from the dilatation effect, $(E_{\text{obs,10K}})_{\text{dila}}$, is estimated after subtracting $(\Delta E/E_0)_{\text{dila}}$ from $E_{\text{obs,10K}}$ and the results are listed in Table 2.

![Graph showing changes in lattice constant and Young modulus](image)
As already mentioned, the Young modulus, $E_0$, expected for a polycrystalline specimen may be found between $\gamma E_0$ and $\delta E_0$ given by (1) and (2), respectively. For the type-L and type-H specimens, the theoretical values at 10 K, $\delta E_{0,10K}$ and $\gamma E_{0,10K}$, may be estimated from the $R_{(hkl)}$ data shown in Fig. 4 and the Young modulus at 10 K, $E_{(100,10K)} = 46.5$ GPa, $E_{(110,10K)} = 88.2$ GPa and $E_{(111,10K)} = 125.7$ GPa, reported for Au metal.\(^{19}\) The results are compiled in Table 2. As seen in Table 2, $(E_{0,10K})_{obs}$ is very close to $\delta E_{0,10K}$ for both the type-L and type-H specimens, and that $\gamma E_{0,10K}$ is much higher than $(E_{0,10K})_{obs}$. It is noted that the Young modulus shows a decrease by about 0.7% and 2.5% for the type-L and type-H specimens after annealing at 800 K, respectively. These decreases in the Young modulus can be explained by the change in the texture after annealing.\(^{17}\) The larger decrease for the type-H specimens is compatible with the fact that the $(100)_\perp$ crystallites become predominant by the grain growth as shown in Fig. 8(b). Since both the 95 K $Q^{-1}$-peak and $Q_{200K}^{-1}$ come to diminish with the progress of the grain growth, they are due to probable anelastic processes in the GB regions. No increase in the Young modulus in spite of these changes by the grain growth may indicate that the Young modulus of the GB region in n-Au is very close to the bulk value. That is, $(E_{0,10K})_{obs}$ is very close to the theoretical value of the Young modulus of the n-Au specimens in which the Young modulus of the GB regions is the same to the bulk value. Further, the fact that $(E_{0,10K})_{obs}$ is very close to $\gamma E_{0,10K}$ for both the type-L and type-H specimens indicates that the theoretical value of the Young modulus of a n-metal specimen can be given by $\delta E_0$. As listed in Table 2, the ratio of $(E_{0,10K})_{obs}/\delta E_{0,10K}$ found is 0.99 and 0.97 for the type-L and the type-H specimens, respectively.

### Table 2 Elastic properties of the n-Au specimens.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$E_{obs,10K}$ (GPa)</th>
<th>$(E_{0,10K})_{obs}$ (GPa)</th>
<th>$\delta E_{0,10K}$ (GPa)</th>
<th>$\gamma E_{0,10K}$ (GPa)</th>
<th>$\gamma E_{0,10K}$/C27</th>
<th>$\delta E_{0,10K}$/C27</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type-L</td>
<td>83 ± 1.5</td>
<td>82.6</td>
<td>93.9</td>
<td>83.4</td>
<td>0.99</td>
<td>0.99</td>
<td>present</td>
</tr>
<tr>
<td>Type-H</td>
<td>78 ± 1.5</td>
<td>77.4</td>
<td>90.4</td>
<td>79.6</td>
<td>0.97</td>
<td>0.97</td>
<td>17(^{17})</td>
</tr>
<tr>
<td>Previous</td>
<td>79 ± 4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>17(^{17})</td>
</tr>
</tbody>
</table>

As already mentioned, the Young modulus, $E_0$, expected for a polycrystalline specimen may be found between $\gamma E_0$ and $\delta E_0$ given by (1) and (2), respectively. For the type-L and type-H specimens, the theoretical values at 10 K, $\delta E_{0,10K}$ and $\gamma E_{0,10K}$, may be estimated from the $R_{(hkl)}$ data shown in Fig. 4 and the Young modulus at 10 K, $E_{(100,10K)} = 46.5$ GPa, $E_{(110,10K)} = 88.2$ GPa and $E_{(111,10K)} = 125.7$ GPa, reported for Au metal.\(^{19}\) The results are compiled in Table 2. As seen in Table 2, $(E_{0,10K})_{obs}$ is very close to $\delta E_{0,10K}$ for both the type-L and type-H specimens, and that $\gamma E_{0,10K}$ is much higher than $(E_{0,10K})_{obs}$. It is noted that the Young modulus shows a decrease by about 0.7% and 2.5% for the type-L and type-H specimens after annealing at 800 K, respectively. These decreases in the Young modulus can be explained by the change in the texture after annealing.\(^{17}\) The larger decrease for the type-H specimens is compatible with the fact that the $(100)_\perp$ crystallites become predominant by the grain growth as shown in Fig. 8(b). Since both the 95 K $Q^{-1}$-peak and $Q_{200K}^{-1}$ come to diminish with the progress of the grain growth, they are due to probable anelastic processes in the GB regions. No increase in the Young modulus in spite of these changes by the grain growth may indicate that the Young modulus of the GB region in n-Au is very close to the bulk value. That is, $(E_{0,10K})_{obs}$ is very close to the theoretical value of the Young modulus of the n-Au specimens in which the Young modulus of the GB regions is the same to the bulk value. Further, the fact that $(E_{0,10K})_{obs}$ is very close to $\gamma E_{0,10K}$ for both the type-L and type-H specimens indicates that the theoretical value of the Young modulus of a n-metal specimen can be given by $\delta E_0$. As listed in Table 2, the ratio of $(E_{0,10K})_{obs}/\delta E_{0,10K}$ found is 0.99 and 0.97 for the type-L and the type-H specimens, respectively.

### 5. Conclusion

The n-Au specimens with the full density were prepared by means of the gas deposition method. The XRD spectra indicate that ultrafine Au particles undergo some rearrangement on the specimen flat-surfaces just after landing during the deposition. Two types of n-Au specimens are prepared as a function of the deposition rate, the type-H specimens above 800 nm/s and the type-L specimens below 800 nm/s. We surmise that the rearrangement of the n-Au particles on the specimen surfaces is not completed for the type-H specimens. The grain growth starts between 300 K and 400 K for the type-H specimens and between 400 K and 500 K for the type-L specimens, respectively. Preliminary DSC measurements show a continuous energy release by $(5 ± 2) × 10^2$ J/mol between 350 K and 750 K for both the type-H and type-L specimens. The GB energy estimated is $(0.3 ± 0.15)$ J/m$^2$ which is comparable with $0.45$ J/m$^2$ reported for bulk p-Au. The concentration of excess vacancy type defects, $C_v$, appears to increase to about $15 × 10^{-4}$ due to the complementary decrease in internal strains after annealing at 400 K, where an atomic volume of the vacancy type defects is assumed to be that of a lattice vacancy. $C_v$ decreases with increasing annealing temperature and diminish after annealing at 800 K. For the mechanical property, it is indicated that the Young modulus of the grain boundary regions is comparable with that of bulk Au. The Young modulus of both the type-L and -H specimens shows a decrease from the parallelism with that of the poly-Au above 200 K due to the anelastic processes in the GB regions.

### Acknowledgments

The authors indebted to Prof. Y. Shirai at Osaka University for the positron life time studies. This work is partly supported by the Center for Tsukuba Advanced Research Alliance (TARA) at University of Tsukuba, a Grant in Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan, and High Damping Materials Project of “Research for the Future” of Japan Society for the Promotion of Science.

### REFERENCES

17. G. Simmons and H. Wang: Single Crystal Constants and Calculated