Nanoscale Mechanical Properties of Ultrahigh-Purity Aluminum*1

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Nanoindentation data reveal interesting behavior in aluminum with various purities: 99.9999% (6N), 99.99% (4N), and 99% (2N). Nanoindentation is used to investigate the relationship between the purity and the mechanical properties of ultrahigh-purity aluminum at room temperature. The area subjected to nanoindentation would be expected to behave similarly to a perfect, dislocation-free single crystal. Nanoindentation data is also compared with results of conventional tensile and hardness tests. These results highlight the differences between microscopic and macroscopic properties. The tensile strength and the hardness of normal-purity aluminum, 99% (2N), are larger than those of ultrahigh-purity aluminum, 99.9999% (6N), and high-purity aluminum, 99.99% (4N). However, in the nanoindentation test, the penetration depth for ultrahigh-purity aluminum (6N) and high-purity aluminum (4N) is less than that for normal-purity aluminum (2N). Thus, microscopic mechanical properties differ from macroscopic mechanical properties. It is suggested that the surface of high-purity aluminum is harder than that of normal-purity aluminum on the micro-scale. The experimental result shows that the perfect crystals are harder than the imperfect crystals. Furthermore, some recovery of the indentation mark is observed in high-purity aluminum. It comes from the recovery of deformation by indentation due to the mobility of defects in the sample.

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1. Introduction

Mechanical and physical properties of materials are very sensitive to the presence of impurities even in trace amounts. Therefore, several research studies to obtain ultrahigh-purity aluminum and to reveal the properties of highly perfect aluminum have been reported.1,2 Using ultrahigh-purity aluminum, the purity dependence of corrosion,3 ballistic effect of conduction electrons4 and slowing down of generation rate of thermal vacancy5 have been investigated. It has been revealed that the physical properties of ultrahigh-purity aluminum are different from those of commercial-purity aluminum. However, mechanical properties, such as tensile strength and hardness, are still unclear.

For the development of materials, it is becoming essential to understand the microscopic structures such as crystal grains and inclusions in the material. Therefore, mechanical properties at nanoscale have become noteworthy, and nanoindentation test has become available for exploring material response near the atomic level.6 The recent numerous nanoindentation studies have revealed that the hardness of a metallic crystal changes with the penetration depth.7–13 It has been clarified that an understanding of the atomic-level processes must be obtained in detail.14–16 In these studies, several properties were obtained from materials with a commercial purity up to 99.99%. However, the mechanical properties of metals, such as hardness, yield stress and so on, are affected by impurities. Hence, in the present work, ultrahigh-purity aluminum was used as sample to make clear the impurity effects. Furthermore, the nanoindentation experiment shows that the hardness increases with decrease of the penetration depth. So, the nanoindentation test was tried using the depth less than 100 nm in order to verify the nanoscale mechanical property.

2. Experimental Procedures

2.1 Sample

The starting material used in this work was 99.999% (5N) pure aluminum produced in Sumitomo Chemical Co., Ltd. with a residual resistance ratio in bulk of about 5000. This material was zone refined in a vacuum between 1 × 10−4 Pa and 1 × 10−5 Pa. This refining was repeated 8 times, and the residual resistance ratio was improved to about 30000 (purity: 99.9999%). In order to clear the purity dependence of the mechanical properties, commercial purity aluminums 4N (99.99%) and 2N (99%) were used in addition to the high-purity aluminums.

All samples were electropolished in a solution of 4C2H5OH + HClO4 for 3 min at an electrode voltage of 17 V, and were annealed at 500°C for 5 h in a vacuum of 2 × 10−5 Pa. Furthermore, 6N and 4N samples were cyclically annealed between 90°C and 300°C 8 times in a vacuum of 2 × 10−5 Pa. The dislocation density in ultrahigh-purity aluminum was 1 × 107 m−2 after cyclic annealing.17

To estimate the average grain size and the dislocation density, these samples were etched for 20 to 30 s in a solution of HCl + HNO3. The measurement of grain size was performed using an optical microscope. The grain sizes of these samples are 0.12 mm for 2N, 1.5 mm for 4N and 3.2 mm for 6N, and the micrographs are shown in Figs. 1(a), (b) and (c). The micrographs of scanning electron microscope are shown in Figs. 2(a) and (b). In these figures, etch pits are recognized clearly, and correspond to dislocation.5

The dislocation density is about 1 × 107 m−2 in the surface of the 6N sample and about 1 × 106 m−2 in the surface of the 4N sample. In the 2N sample, the etch pit becomes unclear due to overall corrosion, but it is inferred that the density of
the 2N sample is fairly higher than that in the 4N and 6N samples.

2.2 Hardness test and tensile test

A hardness tester (Matsuzawa Co., Ltd.) was used for indentation hardness measurements. The Berkovich tip used for the indentation was a triangular pyramid with an apex angle of 60 deg and a tip radius of 0.1 μm. The indentation loads were in the range between 0.05N and 0.5N, and the indentation speed was 30 μm s\(^{-1}\). The dwell time at the selected maximum load was 10 s for each indentation. Hardness test was performed at room temperature. Each sample was indented from five to eight times for each load. Furthermore, each indented point was separated from the others by a distance of more than five times of the indentation mark size.

The tensile test was carried out using a precision universal tester (Shimadzu Co., Ltd.) with a crosshead speed of 0.1 mm min\(^{-1}\) at room temperature. The tensile sample has a gauge length of 20 mm and a gauge cross section of 1 × 3 mm\(^2\) as shown in Fig. 3.

2.3 Nanoindentation test

The nanoindentation function is added to the scanning probe microscope (SPM), Nanoscope III system, made by Digital Instrument Inc. Indentation can be performed with forces between 1 μN and 100 μN. The sample surfaces after indentation can be observed with high resolution. The configuration of the Berkovich tip with a metal foil cantilever is shown in Fig. 4. The cantilever has a length, width and thickness of 350, 100 and 13 μm, respectively, a spring constant of 263 N m\(^{-1}\), and a resonant frequency of 50 kHz.
The diamond tip mounted on the end of the cantilever has a point with a radius less than 25 nm to ensure high imaging resolution and nanometer-scale indentation. The diamond Berkovich tip is a triangular pyramid with an apex angle of 60° and height of 100 μm. To produce highly symmetric indentations, the tip is mounted such that the vertical axis of the pyramid is approximately normal to the sample surface when mounted on the SPM head. In order to make the indentation mark to be equilateral triangle, the angle of the cantilever relative to the sample surface must be adjusted to 22°/3 when indentation is performed at between 19 and 63 mN.

The surface condition of the sample was carefully observed before the nanoindentation test. The initial surface condition of the 6N sample is shown in Fig. 5. A peak to valley of the sample was about 3 nm in over area of 2 × 2 μm² – 3 × 3 μm².

The sample was indented from five to eight times for each load. The magnitude of the indentation load was increased stepwise by 3 mN from 19 to 64 μN. Each indented point was separated from others by a distance of more than five times of the indentation mark size so as to avoid the influence of the previous indentation mark. Figure 6 shows the indentation mark formed on the sample surface after indentation with a load of 44.7 μN. It can be confirmed that it has a clear triangular form.

3. Experimental Results

3.1 Hardness test and tensile test

Results of the hardness test for aluminum with various purities are shown in Fig. 7. It is clear that the penetration depth increases with increasing indentation load, and the depths in the 4N and 6N samples are larger than that in the 2N sample. Therefore, the latter is harder than the former.
However, the penetration depths are almost the same for 4N and 6N. It is considered that the physical meaning of the hardness is related to the yield stress of materials.

Figure 8 shows the stress–strain curves of aluminum with various purities. The tensile strength of 2N aluminum shows a value three times as high as those of 4N and 6N aluminum. This result is consistent with the result of the hardness test.

In the macroscopic mechanical properties obtained for aluminum with various purities, the increase of purity results in decreases of the hardness and the tensile strength. However, it is difficult to detect the difference in hardness or tensile strength between 4N and 6N aluminum in the macroscopic testing.

### 3.2 Nanoindentation test

In the nanoindentation test, penetration depth was less than 100 nm, because the indentation load was on the order of μN. To obtain precise measurements at every indentation load, the nanoindentation test was repeated many times under the same conditions. Figure 9 illustrates the amount of fluctuation of the measured values for (a) 2N, (b) 4N and (c) 6N samples, respectively. The measured values on the 2N sample vary more widely than those on 4N and 6N samples. The fluctuation in the 2N sample is possibly caused by the dislocation density, the grain boundary and the impurity.

The average values of several measurements are shown in Fig. 10. The plots for the 2N sample are above those for 4N and 6N samples. This means that high-purity aluminum, 4N and 6N, is harder than lower purity aluminum 2N. Furthermore, the indentation mark in the 2N sample was observed at indentation loads of 19 and 22 μN, but the indentation mark was not recognized in 4N and 6N samples at the same indentation loads. Regarding the results for the 4N and 6N samples, the penetration depth changes as a function of the indentation load in a complex manner. The penetration depth increase with the increasing indentation load, but in 4N and 6N samples, decreases at about 30 and 55 μN, respectively.

### 4. Discussion

#### 4.1 Hardness test and tensile test

The tensile strength of the 2N sample shows a value three times as high as those of 4N and 6N aluminum. This result is consistent with the result of the hardness test. In the macroscopic mechanical properties obtained for aluminum with various purities, the increase of purity results in decreases of the hardness and the tensile strength. However, it is difficult to detect the difference in hardness or tensile strength between 4N and 6N aluminum in the macroscopic testing.
times larger than those of 4N and 6N samples. This result is consistent with the result of the hardness test. This fact shows that the existence of impurity accelerates the work hardening of a sample. It is widely known that the mechanical properties, such as the hardness and the yield stress, of metals and alloys are affected by their grain size in accordance with Hall–Petch relations. The grain size of the 2N sample was determined to be about 0.12 mm, whereas the grain sizes of 4N and 6N samples were determined to be 1.5 and 3.2 mm, respectively, from the microscopic observation after the chemical etching. On the other hand, dislocation motion is disturbed by the existence of impurities, so that the pile-up of dislocation set up rapidly in low purity metals. In high-purity metals, the pile-up of dislocations is delayed, and work hardening is also delayed.

Remarkable differences between the 4N and 6N samples were not found in the macroscopic hardness test and the tensile test as described above. However, the considerable difference in the impurity content should have any effects on the mechanical property, so that the present study was progressed to the nanoscale test.

4.2 Nanoindentation test

Figure 11 shows the relationship between the indentation load and the penetration depth in the nanoindentation test (Fig. 9) and the hardness test (Fig. 7). The indentation load in the nanoindentation test is three orders of magnitude lower than those in the hardness test. In the hardness test, the hardness that is obtained from the indentation load divided by the projected area is of a magnitude of about 10^2 MPa. The penetration depth for the 2N sample is the shallowest. The results of the hardness test agree with those of the tensile test. However, the hardness estimated by the nanoindentation is of a magnitude of about 10^3 MPa. The penetration depths for 6N and 4N samples are less than that for the 2N sample, that is, the hardness of 6N and 4N samples is larger than that of the 2N sample. High-purity aluminum, 4N and 6N, probably has higher strength than normal-purity aluminum, 2N, in microscopic scale.

As described above, the hardness of high-purity aluminum is less than those of normal-purity aluminum in macroscopic scale. However, 4N and 6N shows higher strength than 2N, because nanoindentation is performed in a microscopic scale.

Since the initial dislocation separation in the 4N and 6N samples is about 30 and 300 μm, respectively. Therefore, the area under nanoindentation is considered to be dislocation free region. So, the high stress is necessary to create a dislocation in such region. This is the reason for the experimental result that the high-purity aluminum has higher strength than that for normal-purity sample in the nanoindentation. Similar experiments have been reported on Au by S. G. Corcoran et al. and J. D. Kiely et al., Ag by G. M. Pharr et al., and Fe–3%Si by D. F. Bahr et al. In these experiments, the strength of material increased with decrease of the penetration depth, and approach to the ideal strength. Nanoindentation experiment for aluminum is scarcely at the present. W. C. Oliver et al. performed using a single crystal aluminum (99.995%), under the measurement conditions of maximum load of 120 mN and maximum penetration depth of 5000 nm, and obtained the hardness of 100–200 MPa. These hardness measures are taken to be almost the same as the present results shown in Fig. 7. In the nanoindentation results, on the other hand, with a penetration depth 10 nm, hardness of about 8000 MPa was obtained, and with a penetration depth of 40 nm, hardness of about 3000 MPa was obtained. The hardness for nanoindentation was obtained from a projected area measured using the SPM function to obtain accurate shapes and sizes. Because of the difference in the indenter tip radius and shape, it is difficult to quantitatively compare these results with reported hardness data.

Figure 10 shows that the penetration depth in the 6N and 4N sample decreases at around 55 and 30 μN, respectively, with increasing indentation load. This complicated behavior is due to the mobility of defects in the sample. The penetration depth changed with time after the nanoindentation, as shown in Fig. 12. Figures 13(a) and (b) show indentation mark shapes at 4 and 17 min after the nanoindentation test was performed with a load of 48.7 μN. The indentation mark shapes changed from a convex to a concave form, so as to observe easily. After 17 min the indentation mark was indistinct, whereas the mark was still sharp after 4 min. It is clear that the top and ridgeline of the indentation marks become rounded. The indentation mark in the 6N sample changes obviously with time at room temperature. Therefore, it is concluded that deformation recovery of the
indentation mark is one of reasons that the penetration depths in the 6N and 4N samples are less than that in the 2N sample. The volume of the indentation mark can be obtained by measuring its side length and penetration depth of the indentation mark, and is shown in Fig. 14 with the distribution of impurities for (a) 6N, (b) 4N and (c) 2N samples at 41.7 μN. The indentation volume of aluminum was $2.9 \times 10^4$ nm$^3$ for 6N, $6.0 \times 10^3$ nm$^3$ for 4N, and $5.5 \times 10^4$ nm$^3$ for 2N. The occupation volume of one impurity was determined from the concentration of impurities as $1.7 \times 10^4$ nm$^3$ for 6N, $1.7 \times 10^5$ nm$^3$ for 4N, and $1.7 \times 10^4$ nm$^3$ for 2N. Hence, the average number of impurities in the indentation volume could be calculated as the indentation volume divided by the occupation volume of one impurity. The average number of impurities in the indentation volume is about 0 or 1 for 6N aluminum, about 25 for 4N aluminum, and about 24000 for 2N aluminum. In 2N aluminum, a great number of impurities exist in the area subjected to nanoindentation. Therefore, work hardening occurs due to the pile-up of the introduced dislocations. On the other hand, in high-purity aluminum, dislocations are introduced by the indentation, but these are easily annihilated, because impurity concentration is less so the dislocation moves more easily. This recovery process is also attributed to the migration of point defect introduced by the indentation. Furthermore, indentation load for which recovery occurs increases with purity. This is explainable as follow. The initiation of dislocation recovery requires an amount of accumulation of dislocation. The accumulation is accelerated by the existence of impurities as described previously. So, in pure sample, higher indentation load needs to start the recovery process.

In the conventional tensile test and hardness test used to evaluate macroscopic properties, the deformation area is the order of micrometer or millimeter, while in the nanoindentation test used to evaluate microscopic properties, the deformation area is the order of nanometer. Such a small area under the nanoindentation is considered to be near perfect crystal. Therefore, the mechanical properties approach to the ideal strength. Furthermore, recovery of the indentation mark in high-purity aluminum was observed, which is caused by the mobility or the disappearance of defects. In future, we will clarify the effect of impurities on the mechanical properties of ultrahigh-purity aluminum by nanoindentation testing in which penetration load–displacement curves can be measured. Furthermore, in this study, the effect of an oxide
layer was not investigated, but it must be examined in near future.

5. Conclusions

To elucidate the mechanical properties of ultrahigh-purity aluminum, the purity dependence of mechanical properties was investigated. Remarkable results are summarized as follows.

1. Zone melting was performed by induction heating in a vacuum of $1 \times 10^{-4} - 1 \times 10^{-5}$ Pa. Ultrahigh-purity aluminum (purity: 99.9999%) with a residual resistance ratio of about 30000 was obtained after the aluminum rod was zone-melted 8 times.

2. The tensile strength and the hardness of normal-purity aluminum (99% (2N)) are higher than those of ultrahigh-purity aluminum (99.9999% (6N)) and high-purity aluminum (99.99% (4N)).

3. In the nanoindentation test, the penetration depths in ultrahigh-purity aluminum (6N) and high-purity aluminum (4N) were less than that in normal-purity aluminum (2N). The area subjected to nanoindentation is expected to behave as a perfect crystal in high-purity aluminum. Therefore, the experimental result indicates that the perfect crystals are harder than the imperfect crystals.

4. Some recovery of the indentation mark was observed in high-purity aluminum. It comes from the recovery of deformation by indentation due to the mobility or the disappearance of defects in the sample.

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REFERENCES