Nanoindentation measurement of hardness and modulus anisotropy in Ni$_3$Al single crystals

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Hardness and elastic modulus of (111), (110), and (001) oriented Ni$_3$Al single crystals were determined by nanoindenter measurements. Obvious elastic modulus anisotropy and hardness anisotropy were observed. The modulus for (001) was about 17% smaller than that for (111), (110). The hardness was found to be strongly dependent on the indentation size and exhibited a small anisotropy at low indentation loads. When the indentation load was increased further, the hardness anisotropy became apparent. The hardness for (111) was observed to be higher compared to (001). The indentation hardness size effect was examined by using strain gradient plasticity theory.

I. INTRODUCTION

The depth-sensing nanoindentation technique has been widely used for determining mechanical properties of bulk materials and thin films. Two mechanical properties most frequently measured using this technique are elastic modulus and hardness. Elastic modulus is one of the important material constants, which is related to the microstructure and mechanical performance of the material. Many metals exhibited elastic anisotropy when indentation tests were conducted on different crystallographic planes. In addition to the elastic anisotropy, hardness anisotropy is often observed in crystals due to resolved shear stress needed for the motivation of slide systems on different crystallographic planes. However, because of the phenomenon of the indentation size effect (ISE)—the dependence of hardness on the applied load, the obtained results are not well understood in some cases and materials, involving confusing interpretations and discussion. There are ample data in the literature showing a size dependence of the measured hardness when the indent size is in the range of 0.1 to 10 μm. Generally, it is observed that hardness of a material increases as the indent size decreases. However, in some cases no significant size dependence was observed or the indentation hardness was even found to increase with an increasing indenter load. These controversial results are obviously difficult to interpret by conventional plasticity theory. It has been suggested that this disagreement is the result of the invalidity of the two-dimensional slip-line theory, since the indenter used for hardness testing is three-dimensional. Recently, some investigators have used strain gradient plasticity and the concept of geometrically necessary dislocations to explain the variation in the indentation hardness of the test materials. In this theory, the geometrically necessary dislocations required for compatibility reasons due to the presence of strain gradient affects the yield stress in a manner similar to common statistically stored dislocations. For a sharp, constant angle indenter, like a Berkovich, or Vickers indenter, the density of the geometrically necessary dislocations is assumed to be proportional to plastic strain. Nix and Gao predict a linear dependence of the square of hardness on the inverse of the indentation depth. Some single crystals and polycrystalline metals data were found to agree with this linear relationship.

In the present paper, indentation results were obtained using a continuous loading indenter system applied to three oriented (111), (110), and (001) Ni$_3$Al single crystals. The elastic modulus and hardness anisotropy as well as its evolution with indentation size were explored.

II. EXPERIMENTAL

Ni$_3$Al(B) (Ni–75.6 at.%, Al–23.9 at.%, and B–0.5 at.%) single crystals used in this work were grown using the Bridgman technique. The crystal was cut into rectangular-shape specimens, which were annealed in Ar at 1523 K for 14 days, cooled down at a rate of 1 K/min to reduce the dislocation density. After mechanical polishing, Ni$_3$Al crystals were electropolished at room temperature using a mixture of acetic acid, nitric acid, and...
muriatic acid with a volume ratio of 8:4:1. The surface morphology of the samples was examined with a scanning tunneling microscope (STM) operating in the contact mode. The STM tips used were made of single crystals of silicon nitride. The STM image was conducted in air under appropriate feedback and bias voltage conditions. Figure 1 shows a typical STM image of (111) Ni₃Al crystal. The surface roughness is below 8 nm. X-ray photoelectron spectroscopy (XPS) analysis was employed to determine the surface structure of the samples. XPS results show that about 4-nm-thick oxide and hydroxide layers exist on the electropolished sample surface.

The nanoindentation experiments were performed using a nanoindenter XP (MTS, Hunt Valley, MD) fitted with a three-sided pyramid Berkovich indenter. The loading and unloading sequences are standard. After the tip approached the surface at 10 nm/s, the indenter was loaded at constant loading (or strain rate) to a peak load, then held at the constant load for 10 s, unloaded to 10% of the peak load, held for 60 s, and finally completely unloaded.

During indentation, one edge of the triangular indenter was oriented parallel to fixed crystal orientation of the samples to obtain comparative results. The position of the indenter was also rotated to different angles according to the symmetry of the crystals. The indenter orientations on the respective crystallographic planes are shown in Fig. 2. The “normal” (N) denotes one indenter edge parallel to [112], [001], and [110] directions for (111), (110), and (001) crystals, respectively. The “rotation” (R) symbolizes the indenter rotates clockwise at angles of 30°, 90°, and 45° for three samples.

Tests were conducted at different loads using a constant loading rate of 5% of the peak load. Two sets of indents were made for each orientation with nominal loads of 5 and 100 mN in each set. For each specimen, at least 35 indents were made. The results given here represent the averages for the group. The load–displacement data obtained during the final unloading were analyzed using the method of Oliver and Pharr¹ to determine the hardness and elastic modulus. The hardness \( H \) is calculated from the actual contact area \( A_C \) and maximum load, \( P \):

\[
H = \frac{P}{A_C}.
\]

The reduced modulus \( E_r \), which accounts for elastic displacement in both the specimen and indenter, is evaluated from

\[
E_r = \frac{1}{\beta} \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A_C}},
\]

where \( \beta \) is a constant with a value of 1.034 for a Berkovich indenter, \( S \) is contact stiffness determined by curve fitting the upper portion of the unloading curve and measuring it slope at peak load. \( A_C \) is contact area and can be deduced from an empirically determined shape function. The elastic modulus of the specimen \( E \) is extracted from the effective modulus using

\[
\frac{1}{E} = \frac{1 - \nu^2}{E} + \frac{1 - \nu_i^2}{E_i}.
\]

where \( E_i \) is modulus of indenter, and \( \nu \) and \( \nu_i \) are Poisson’s ratio for the specimen and the indenter, respectively. The values \( E_i = 1141 \) GPa, \( \nu_i = 0.07 \), and \( \nu = 0.29 \) are used in all the computation here.

The hardness–depth relationship was obtained using continuous stiffness measurement (CSM) with a dynamic technique. The tests were conducted at a constant strain of 0.05 to a maximum depth of 1.8 \( \mu \)m. Finally, the indentation impressions were examined by scanning electron micrography (SEM) using JSM-6301F emission instrument operating at 5 kV.

III. RESULTS

Figure 3 shows the typical load–displacement curves at indentation load of 5 mN for three crystallographic planes of Ni₃Al, respectively. In each indentation, the same experimental conditions were used. From the load-displacement curves, the indentation modulus \( (E_r) \) and hardness \( (H) \) values were extracted. The measurement results of \( E_r \) and \( H \) from different indentation tests are summarized in Fig. 3. It shows that the measured data for \( E_r \) and \( H \) are rather consistent with a relatively small standard error for each specimen. The reduced modulus values are \( 199 \pm 10 \), \( 194 \pm 7 \), and \( 174 \pm 8 \) GPa for (111), (110), and (001), respectively. An obvious elastic anisotropy is observed with the lowest modulus value in (001). The hardness values of (111), (110), and (001) are \( 4.63 \pm 0.27 \), \( 4.51 \pm 0.25 \), and \( 4.81 \pm 0.29 \) GPa.

![Fig. 1. STM morphology of the electropolished Ni₃Al (111) surface.](image-url)
respectively. Evidently, the hardness in (001) plane is slightly larger than that in the other two planes at the present experiment condition.

Figure 4 gives the $E_r$ and $H$ values measured at indentation load of 100 mN with a fixed indenter orientation. The results show that the $E_r$ values of (111), (110), and (001) measured at 5 and 100 mN are almost the same. The $H$ values for the three crystals drop remarkably with an increased indentation load to 100 mN, being $3.49 \pm 0.07$, $3.13 \pm 0.22$, and $3.24 \pm 0.04$ GPa for (111), (110) and (001) planes, respectively. The (111) crystal exhibits the highest $H$ value, while (110) is the lowest

![Diagram of crystal orientations](image)

**FIG. 2.** Orientations of the indenter impressions on the index surfaces of Ni$_3$Al single crystals.

![Graphs and plots](image)

**FIG. 3.** Load–displacement curves, hardness, and reduced modulus distribution with indent number of Ni$_3$Al single crystal at indent load of 5 mN (indenter orientation, $N$).
one. These results suggest that these crystals exhibit a clear hardness anisotropy with increasing indentation load. From Fig. 4, we also note that the measured $E_r$ and $H$ values at a high load show smaller scatter values compared with those obtained at low loads.

The indenter orientation effect on the measured $E_r$ and $H$ values was also examined. With the indenter orientation $R$ (shown in Fig. 2), the indentation tests were conducted at 5 and 100 mN, respectively. The measured results are summarized in Figs. 5 and 6. It can be seen that $E_r$ and $H$ values measured at $R$ orientation are the same as those at $N$ orientation. These results indicate that the indenter orientation has little effect on the measured $E_r$ and $H$ values when the tests are conducted at the same indent load. A similar effect had been observed by Lee and his co-workers when indentations were made on B-doped Ni$_3$Al crystals. It was also found that the orientation of the indentation mark has a small effect on the
microhardness measurement. A variation of about 4% was observed as the samples were rotated about their [001] axes parallel to the indentation direction. Obviously, our measurements are consistent with the previous observations.

Figure 7 shows a typical SEM image of 250 mN indentation into (111) crystal. The impression does not show any pileup or sink-in behaviors, which are always observed in some metals when they are subjected to indentations, and can severely influence the measurements of hardness and modulus. Our SEM observation indicates that the directly calculated $E_r$ and $H$ using the unloading curve method do not need any area calibration. The near-edge regions of the indentation show some faint linear traces (as shown by arrows). These traces are slip-lines, which have been observed in the impressions of some semiconductors.15

The CSM tests were conducted on these crystals to investigate the indentation size effect. Figure 8(a) summarizes the measurement results of modulus from three crystallographic planes as a function of penetration depth. It is seen that the $E_r$ value is larger at the top surface; it decreases and tends toward a saturation with an increasing penetration depth up to 200 nm. The saturation $E_r$ values of (111), (110), and (001) planes are 194 ± 13, 191 ± 11, and 173 ± 9 GPa, respectively. These $E_r$ values from CSM are coincident with those obtained from loading–unloading curves (Fig. 3). Figure 8(b) shows the hardness as a function of indentation load for three crystals. The hardness value for each crystal was found to be continuously decreasing with an increasing load, indicating an obvious indentation size effect. The hardness value of (110) is lowest among these three specimens in the whole load range. When the load is below 150 mN, a slight difference in $H$ values for (111) and (110) is seen. When the load is increased further, as shown in Fig. 8, the $H$ value for (111) increases slightly but evidently drops for (001). When the indentation load reaches 250 mN, the $H$ values for (111), (110) and (001), as indicated by the dash line, are 3.44, 3.13, 2.98 GPa, respectively. This shows that the hardness anisotropy is strongly dependent on the indentation load size.

In the literature, the measured and calculated elastic modulus values of Ni$_3$Al monocrystalline are 20316 and 205 GPa,17 respectively. If we convert the measured $E_r$ using the CSM method with Eq. (3) to elastic modulus, the obtained values for (111), (110), and (001) planes are 217 ± 14, 215 ± 14, and 190 ± 10 GPa, respectively. Obviously, our measured modulus results are consistent with these data.

Rao and his co-workers18 have measured the Vickers hardness ($H_V$) of Ni$_{76}$Al$_{24}$ alloys containing various amounts of boron with a load of 100 g. For the 0.5 at.% Ni$_{76}$Al$_{24}$ alloy, the measured $H_V$ value is about 3.6 GPa. Lee reported that the $H_V$ values of B-doped (001) Ni$_3$Al single crystal with both mechanical polishing and chemical etching measured with indentation load of 10 g were in the range of 2.4 to 2.9 GPa.14 Obviously, our measured $H$ values are within the range of those previous measurements. However, the $H_V$ values of the same composition of B-doped Ni$_3$Al alloys with a load of 10 kg reported by Brusso et al. is about 1.8 GPa.19 These results indicate an evident indentation size effect in the Ni$_3$Al alloys.

FIG. 6. Hardness and reduced modulus versus indent number at a load of 100 mN (indenter orientation, R).
IV. DISCUSSION

In terms of the measurement results, one can see that the indentation size effects on the hardness values are different in different crystallographic planes. This observation may imply that the dislocation activities are dependent upon the crystallographic orientations in the Ni$_3$Al crystal.

According to strain gradient plasticity theory, as an indenter is forced into the solid surface, geometrically necessary dislocations are required to account for the permanent shape change at the surface. Using Taylor expression to estimate the shear strength ($\tau$) of the material under the indenter tip, one may have

\[
\tau = CGB\sqrt{\rho_S + \rho_G} ,
\]

where $G$ is shear modulus, $b$ is the magnitude of Burgers vector, and $C$ is constant taken to be 1/3 by Ashby, and $\rho_S$ and $\rho_G$ are the densities of the statistically necessary dislocation and geometrically necessary dislocation. For a metal, the hardness is about three times the flow stress, so the hardness can be written in terms of dislocation densities. Using the von Mises factor of $\sqrt{3}$ and constraint factor of 3, the equation can be expressed as

\[
\left(\frac{H}{H_0}\right)^2 = 1 + \frac{h^*}{h} ,
\]

where $H_0$ is the hardness at infinite depth of indentation

\[
H_0 = 3\sqrt{3CGb}\sqrt{\rho_S} ,
\]

and $h$ is a characteristic depth given by

\[
h^* = \frac{3}{16\rho_S (\cot\theta)^2} ,
\]

where $\theta$ is the angle between the face of indenter and the material surface, and $h$ is the indentation depth. An indentation size dependence of hardness is evident and probably a consequence of the indentation depth.

Figure 9 gives the $H^2$–$h^{-1}$ relationship of three crystals. For (111) plane, its highest load was limited to 150 mN due to a slight increase of hardness value above this load. $H_0$ values for (111), (110), and (001) planes are 3.34, 3.13, 2.98 GPa, respectively. Figure 9 shows clear linear relationships for three orientations supporting the strain gradient plasticity theory of indentation hardness. It suggests that the two components of the dislocation density add in a linear manner with an increasing indentation load. The linearity in Fig. 9 implies that a linear addition law for $\rho_S$ and $\rho_G$ is appropriate. From this figure, it can be seen that the slope is steeper for the (110) and (001) planes than that in the (111) plane, indicating a gradient of strain steeper in those two crystals than that.
in (111). This also suggests that the (111) crystal has a higher work hardening rate, which tends to spread the plasticity over a wide volume.

Previous tensile tests\textsuperscript{21–23} reported that there is a small anisotropy of the flow stress among different Ni\textsubscript{3}Al oriented crystals. That of the sample near the [1\overline{2}11] crystal is 35 MPa stronger than that of those oriented near [001] and [011], and the weakest one is the sample near [011]. Since the measured hardness reflects yield stress, our measurements of hardness anisotropy of three Ni\textsubscript{3}Al crystals are comparable with those of flow stress anisotropy measured in tensile tests. For the (111) plane, the hardness shows a slight increase at higher loads (\(\geq 150\) mN). This behavior indicates a different size effect from that in the other planes. A similar phenomenon has been reported by Norwak and Sakai\textsuperscript{24} for a sapphire crystal in which the hardness increases under higher load. To understand the phenomenon of an increasing hardness with indentation load occurring in Ni\textsubscript{3}Al (111) crystal, more intensive investigations are needed and are in progress.

V. CONCLUSIONS

A nanoindenter was used to quantify the elastic and plastic anisotropy of Ni\textsubscript{3}Al crystals. The indenter orientation has no effect on the hardness and modulus measurement. The results show that the elastic modulus of (001) is about 17% smaller than that of (111) and (110). The measurement hardness apparently shows indentation size effect. This effect is in good agreement with the strain gradient plasticity theory. The hardness exhibits only a small anisotropy at low indentation load. With further increase in indentation load, the hardness anisotropy becomes apparent. The observed hardness anisotropy is consistent with the flow stress anisotropy which was investigated previously by tensile testing.

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