Unusual annealing effects on hardness and strain rate sensitivity of nanocrystalline Nb

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A B S T R A C T

The dependence of microstructure, hardness \( H \) and strain rate sensitivity \( m \) of nanocrystalline (NC) body-centered cubic Nb thin films at various annealed temperature were experimentally evaluated. The annealed temperatures ranged from 100 to 400 °C, and kept for 30 min respectively. Despite nearly unchanged grain sizes upon annealing, the strengthening effect was observed in nanoindentation hardness testing as annealing temperature was increased above 200 °C. In particular, the strain rate sensitivity of NC Nb increased significantly after annealing at 100 °C and slightly decreased at higher annealing temperatures. Competitive mechanisms underlying the different variation trends of hardness and strain rate sensitivity of NC Nb annealed in the two different temperature regimes were proposed.

1. Introduction

Annealing is a common heat treatment method used to alter the microstructure and mechanical properties of crystalline metals. For coarse grained metals, annealing could reduce hardness by decreasing dislocation densities in view of the Taylor relationship \([1,2]\). In contrast, it has been widely accepted that nanocrystalline (NC) metals rarely exhibit strain hardening, due to limited dislocation storage and accumulation in nanoscale grains \([3]\). Nevertheless, numerous studies have revealed that annealed NC metals may exhibit distinct mechanical properties, e.g., crossover from hardening to softening in NC Ni films by grain boundary relaxation after low temperature annealing treatment \([4]\), enhanced ductility of high-strength NC Ni by introducing bimodal grain-size distribution upon annealing \([5]\), and improved strength and decreased flow stress in annealed NC Al by eliminating dislocations mediated plastic deformation \([6]\). Even high strain hardening rate or plasticity of steel by formation of twinning through severe deformation and annealing process was realized \([7]\). Moreover, improving grain boundary stability by annealing was an effective method to derive better mechanical properties NC metals \([8]\).

For body-centered cubic (bcc) metals, specifically, the plastic behaviors of bcc metals were generally dominated by screw dislocation kink-pair nucleation \([9]\). The core structure of sessile 1/2 \langle 111 \rangle screw dislocations of bcc metals is nonplanar and should spread into three \langle 110 \rangle planes of the \langle 111 \rangle zone. Therefore, the movement of screw dislocation could extend in three-dimensional space from one \langle 111 \rangle plane to another \([10]\). Then, the temperature and flow stress dependent flow were the direct results of the nonplanar nature of screw dislocation \([11]\). Especially, when the testing temperature is below a critical temperature \(T_c\), the high Peierls stress of bcc metals leads screw dislocations to move slower than edge dislocations \([12,14]\). \(T_c\) is usually defined as the temperature at which the flow stress becomes insensitive to temperature.

This study aims to investigate the effects of annealing on the microstructure, hardness \( H \) and strain rate sensitivity \( m \) of NC bcc metals. The hardening of hardness \( H \) and a crossover from increasing to decreasing strain rate sensitivity \( m \) of annealed bcc-Nb films were presented and compared to that of as-deposited Nb. Moreover, via nanoindentation testing, the value of \( m \) was found to decrease with increasing annealing temperature for annealed Nb. Therefore, identifying the dominant deformation mechanism and microstructure underlying the unusual properties of annealed Nb becomes the main focus of the present study.

2. Experiments

2.1. Sample preparation

NC Nb thin films (thickness 1000 nm) were deposited on single Si (111) substrates via direct current magnetron sputtering under an argon
pressure of 0.3 Pa at room temperature. The direct current sputtering power of Nb target (99.99% purity) was 100 W, and the deposited rate was ~ 6 nm/min. Four as-deposited Nb films were separately annealed in vacuum at 100 °C, 200 °C, 300 °C and 400 °C, all lower than the re-crystallization temperature about 0.3 $T_m$ ($T_m$ being the melting point, about 2468 °C for Nb), for 30 min. In addition, energy dispersion spectrum (EDS) analysis eliminated the presence of interstitial contaminants introduced from annealing treatment. The high purity of samples excluded the influence of oxidation layer [15] and hydrogen embrittlement [16,17] on the mechanical properties of Nb films.

X-ray diffraction (XRD) was performed using a horizontal General Electric θ-2θ power diffract meter in continue-scanning mode with Cu Kα radiation ($\lambda = 0.154056$ nm), and the scanning rate was 1°/min. The instrumental width arising from the beam broadening was about 0.147°, which was determined by testing a fully annealed coarse-grained silicon powder in the present study. The films were subsequently characterized by high-resolution transmission electron microscopy (HRTEM) using a JEOL JEM-2100F operated at 200 kV. In addition, the thin foils of different samples for TEM observation were respectively prepared and fabricated by ion beam milling technique conducted by Gatan Precision Ion Polishing System.

2.2. Nanoindentation tests

Nanoindentation tests were conducted using Nanoindenter XP* system (MTS, Inc.) under continuous stiffness measurement (CSM) mode, with the loading strain rate (LSR) varied from 0.005 s$^{-1}$ to 0.2 s$^{-1}$. The indentation depth was set at 100 nm (1/10-1/7 film thickness) so as to eliminate potential substrate and surface effects. Berkovich diamond indenter with a nominal tip radius estimated to be ~150 nm was employed. Thermal drift correction was carried out with the indenter unloaded to 10% of the maximum load. To increase the effectiveness of the present experimental measurement, 16 series of test data were obtained at each loading strain rate.

3. Results

Fig. 1 shows the XRD diagram and selected area electron diffraction patterns of the Nb films, confirming no detectable Niobium oxides or hydrides formation upon annealing. Based on the Scherrer-Wilson equation and the derived XRD analysis, interestingly, the average grain sizes of all the annealed Nb films were found to be nearly identical. For example, the plan-view bright-field TEM micrographs shown in Fig. 2 indicated that the average grain size of Nb film annealed at 400 °C was ~81 nm, which was comparable with that of the as-deposited one (~74 nm). Table 1 presents the detailed average grain sizes of testing samples calculated by statistics analysis > 200 grains from TEM micrographs. Fig. 2(c) and (d) also revealed relatively narrow grain size distributions in both the as-deposited and annealed Nb films, indicating no effects of bimodal grain size distribution on the plastic deformation of Nb films. In addition, no twinning was formed during the annealing process either. Furthermore, Fig. 3 demonstrates the cross-sectional bright-field and dark-field TEM photographs for as-deposited (a, d), 100 °C-annealed (b, e) and 400 °C-annealed Nb (c, f), respectively. It showed that the shapes of the observed grains were all column at various annealing temperatures, excluding the contribution derived from different grain morphologies to hardness.

As shown in Fig. 4, compared with the hardness of as-deposited NC Nb, the nearly constant hardness was derived upon annealing at low temperature, below 200 °C, while significantly enhanced hardness was obtained when the film was annealed at temperature equal or above 200 °C. This clearly demonstrated the unusual effects of annealing temperature on the hardness of NC Nb.

It has been well known that dislocation density could be calculated from XRD pattern, based on the Scherrer and Wilson equation [18,19], as:

$$\frac{b^2}{\tan \theta^2} = \frac{\lambda \beta}{d \tan \theta \sin \theta} + 16(\varepsilon)^{1/2}$$

(1)

$$\rho = \frac{2(3)(\varepsilon)^{1/2}}{db}$$

(2)

where $\lambda$ was the wavelength of Cu Kα irradiation, $\theta$ was the peak position, $d$ was the grain size, $b$ was the Burgers vector of Nb, $\beta$ was the integral width of the physical broadening profile determined by $\beta = \int I \sin \theta dB$, and $I$ was the peak intensity. The main peak of (110) was applied to calculate the micro-strain $(\varepsilon)^{1/2}$ and the dislocation density $\rho$. The dislocation densities of Nb thin films thus calculated were represented by blue hexagon icon and dash dot line in Fig. 4, which showed that the dislocation density decreased slightly with increasing

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**Fig. 1.** XRD patterns of as-deposited and annealed Nb films (a), (b) corresponding diffraction patterns.
Table 1
Grain sizes of testing films calculated by statistics analysis from TEM.

<table>
<thead>
<tr>
<th></th>
<th>As-deposited Nb</th>
<th>100 °C-annealed Nb</th>
<th>200 °C-annealed Nb</th>
<th>300 °C-annealed Nb</th>
<th>400 °C-annealed Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain size/nm</td>
<td>74.0 ± 9.00</td>
<td>80.6 ± 8.54</td>
<td>73.7 ± 8.90</td>
<td>75.9 ± 9.60</td>
<td>81.0 ± 9.00</td>
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annealing temperature. Note the order magnitude of $\rho$ was $10^{15}$ m$^{-2}$, which indicated a high density of dislocations remained in the NC Nb. Moreover, the TEM images for the inner grain structures of as-deposited Nb, 100 °C-annealed Nb and 400 °C-annealed Nb (as shown in Fig. 5) also confirmed that the dislocation density decreased with increasing annealing temperature. Also, the red symbol "∟" in the IFFT graphs (Fig. 5(e–f)) represented the pure edge dislocation or mixed dislocation. Then, the flow stress ($\sigma$) and the harness ($H$) could be calculated using the classical Taylor expression [20], as:

\[
\sigma = \sigma_0 + \alpha \rho b \frac{1}{2} \\
H = 3\sigma
\]

(3)

(4)

where $\sigma_0$ was the intrinsic strength without dislocation interactions, $\alpha$ was an empirical constant (which could be expressed by $\alpha = \frac{1}{2\pi(1-\nu)^2}$ [21] and calculated to be about 0.5) and $G$ was the shear modulus. The variation trend of hardness thus calculated was displayed in Fig. 4 using red triangular icon and dash dot line.

In addition to hardness, the strain rate sensitivity ($m$) of the Nb thin films was estimated using Eq. (5). First, the strain rate sensitivity is defined as the variation of hardness with loading strain rate, expressed as [22]:

\[
m = \frac{\partial \ln H}{\partial \ln \dot{\varepsilon}}
\]

(5)

where $H$ and $\dot{\varepsilon}$ are the hardness of Nb and the corresponding loading strain rate upon nanoindentation, respectively. Then, the value of $m$ was calculated from typical double logarithmic curve of hardness versus loading strain rate as shown in Fig. 6. The as-deposited Nb had the smallest $m$ value of 0.014, which is consistent with $m < 0.1$ for BCC metals [23]. As the annealing temperature was increased, the value of $m$ decreased from 0.038 to 0.023 in the current study.
4. Discussion

Upon annealing treatment, strengthening and softening in NC metals were both reported. A multitude of mechanisms such as dislocation starvation [24,25], grain-boundary (GB) relaxation [4,6,26] and forest dislocation strength [14] were proposed to dominate plastic deformation under different circumstances. Intriguingly, in the present NC Nb, strengthening appeared as the annealing temperature above 200 °C, and the hardness kept almost constant below this temperature. Importantly, as shown in Fig. 6, the strain rate sensitivities of annealed films were all higher than that of as-deposited Nb, which is contrary to the previous results obtained for FCC-Ni [4].

As shown in Figs. 4 and 6, two regimes could be identified for temperature dependent hardness and strain rate sensitivity. Relative to as-deposited NC Nb, upon annealing below 200 °C, the hardness of Nb100 and Nb200 became slightly lower while their strain rate sensitivity increased appreciably. However, increasing further the annealing temperature from 200 to 400 °C led to opposite variation trend, as the hardness increased while the strain rate sensitivity decreased. In the sections to follow, the scenarios corresponding to the underlying deformation mechanisms as well as the related microstructural evolution processes in the two temperature regimes are discussed.

4.1. Hardness

Upon annealing treatment, two competing processes, i.e., dislocation annihilation and grain boundary (GB) turning homogeneous, would occur simultaneously in NC Nb, and the two processes may affect the hardness of NC Nb in different ways. As shown in Fig. 4, dislocation density decreased continuously with increasing annealing temperature, which should reduce the hardness. However, the dislocation density changed insignificantly, and then the hardness decreased slightly even nearly constant at low annealing temperature. In addition, as GBs in nanocrystalline materials are known to be effective sources for dislocation nucleation/annihilation, the hardness should also be dependent on the structure of GBs. Therefore, GBs in NC Nb were continuously changed to become homogeneous, which eliminated GB ledges and defect debris located within the GB effective zone and reduced the intrinsic stress [27]. Correspondingly, the stress required for dislocation nucleation should increase, due to the lacking of GB ledges and the reduced intrinsic stress around GBs. As a result, contrary to the weakening effect of dislocation annihilation, homogenized GBs upon annealing should strengthen the hardness of NC Nb.

The homogenized process of GBs upon annealing was captured by HRTEM images shown in Fig. 7, which revealed the morphologies of GB structure in the current NC Nb samples. As the GB structure was closely related to boundary misorientation, therefore, identical low-angle boundary which had same misorientation angle of 15.2°, in order to rule out the possible differences among GBs. As shown in Fig. 7, GBs in as-deposited and 100 °C-annealed Nb were relatively disordered, as their width (~3.4 ± 0.5 nm) were wider than that in 300 °C-annealed Nb (~2.4 ± 0.4 nm). With increasing annealing temperature, the GB affected zone became more organized. For example, the GBs in as-deposited and 100 °C-annealed Nb contained discontinuous lattice fringes structures and the atoms arranged loosely, while the regularly atoms and spaced GB dislocations existed in the 300 °C-annealed-Nb. Also, Fig. 8 showed the similar high-angle boundary (~26.3°) of as-deposited (a) and 300 °C-annealed Nb (c). From the corresponding IFFT graphs (c, d), ledges could be identified in the GB region of as-deposited NC Nb (c), which were effectively eliminated via annealing as shown in 300 °C-annealed Nb (d). Furthermore, a visual model diagram was offered to interpret the “organized” as shown in Fig. 9. The two processes as proposed above competed with each other as the annealing temperature was increased, resulting in annealing temperature dependent hardness shown in Fig. 4.

Apparently, the calculated hardness based on dislocation density is consistent with the experiments results when annealing temperature below 200 °C as shown in regime 1 of Fig. 4, suggesting the dominant mechanism might be GB-dislocation related mechanisms. As the annealing temperature was increased above 200 °C (regime 2 of Fig. 4), even though the dislocation density decreased continuously, the reduction in hardness due to decreasing dislocation density was compensated by the higher stress required to nucleate dislocations from homogenized GBs. Eventually, at annealing temperature of 300 and 400 °C, the enhancement in hardness derived from homogenized GBs could be much larger than hardness drop as a result of decreased dislocation density.

4.2. Strain rate sensitivity

Intriguingly, the strain rate sensitivity m increased dramatically from as-deposited NC Nb to the one annealed at only 100 °C (Fig. 6), despite the nearly unchanged grain size upon annealing. It had been proposed that the higher strain rate sensitivity in BCC metals was in general closely related to the motion of screw dislocations. For coarse grained BCC metals, the slip process of screw dislocations dominates their plastic deformation, causing thence high strain rate sensitivity. With deceasing grain size, the dislocation density changed in different ways for edge dislocations, screw dislocations and mixed dislocations having both edge and screw components [28].

For NC bcc metals, i.e., Mo, it had been suggested that the density of pure screw dislocations monotonically decreased as grain size d decreased, and nearly disappeared as d became smaller than 100 nm, while only pure edge and mixed dislocations remained when 30 nm < d < 100 nm [28]. Note that the grain sizes of the present NC Nb samples were all within the range of 74–81 nm, thus within the range of 30 to 100 nm proposed above for BCC metals. Therefore, it might be reasonable to assume that dislocations in as-deposited NC Nb were pure edge and mixed ones, without pure screw dislocations. This may explain why the strain rate sensitivity of as-deposited NC Nb was relatively small, consistent with the trend reported previously for BCC metals [29].

4.2.1. Regime of lower annealing temperature

After annealing at 100 °C, the strain rate sensitivity of NC Nb increased dramatically from ~0.014 to ~0.038. Such dramatic increase of m was unexpected, as the changed dislocation density and the nearly unchanged grain size of NC Nb could not explain the variation trend of m upon annealing. With regard to dislocations, as mentioned above, screw dislocations hardly exist in BCC metals with grain size smaller
than 100 nm, and the densities of pre-existing pure edge dislocations and mixed dislocations should decrease during the annealing process. Concerning screw dislocations, however, there existed a critical temperature $T_c$ (~350 K for Nb [14,30,31], lower than all the annealing temperatures presented), above which screw dislocations exhibited identical motion rate with edge dislocations [32]. Then, the nucleation rate of kink-pair reached its migration rate when the temperature was higher than $T_c$ [33–35]. Moreover, MD simulations have confirmed the image forces on a screw dislocation could act in opposite directions on either end of the dislocation, which could cause the cross-slip and result in the self-pinning/generation of dislocations [36,37]. Therefore, upon annealing, as the vacancies and atoms rearranged to reduce the lattice.
energy by thermal effect, the pure edge dislocations glided and should be easily annihilated at GBs [6], while mixed dislocations should be preserved in annealed state Nb. This was also the reason that dislocation starvation could hardly observe in NC BCC metals, or micro/nanoscale BCC pillars [38].

In addition, the strain rate sensitivity of flow stress could be expressed as [9]:

\[ m = \frac{\Delta \ln \tau}{\Delta \ln \dot{\gamma}} \]  

(6)

where \( \tau \) is the shear stress and \( \dot{\gamma} \) is the shear strain rate obtained by:

\[ \dot{\gamma} = b_\varepsilon \rho_\varepsilon v_\varepsilon + b_s \rho_s v_s \]  

(7)

where \( b \) is the Burgers vector, \( v \) is the motion rate of dislocation, and \( \rho \) is the dislocation density. Meanwhile, the subscripts \( \varepsilon \) and \( s \) represent the edge and screw component/dislocation, respectively. Accordingly, the large amount of pure edge dislocation density \( (\rho_\varepsilon) \) and its faster mobility rate \( (v_\varepsilon) \) in as-deposited Nb should result in lower value of \( m \) than that of the annealed one. While the contribution to the strain rate sensitivity of annealed Nb by mixed dislocations, the slower mobility rate of the screw component \( (v_s) \) determined the movement of mixed dislocation, which should lead to higher \( m \) based on Eq. (7). Nevertheless, the screw component/dislocation density \( (\rho_s) \) was proportional to the total dislocation density as shown in Fig. 4, therefore the \( m \) should decrease with annealing temperature. Alternatively, as the grain size of NC Nb remained nearly unchanged upon annealing, the attribution of strain rate sensitivity derived from refined grain size in BCC metals [35] was also not applicable. Other mechanism(s), i.e., microstructure evolution and related stress distribution should not be eliminated either.

As the grain size is reduced to nanoscale, GB related deformation mechanisms, e.g., GB sliding and GB diffusion, may increasingly contribute to the plastic deformation of NC BCC metals, leading therefore to higher strain rate sensitivity. Specifically, it was proposed that GB sliding is a stress dependent process, whose contribution to plastic deformation increases with decreasing intrinsic stress [36]. Therefore, the more homogeneous GBs with much less ledges and lower intrinsic stress in NC Nb derived after annealing process might enhance sliding compatibility between neighboring nanoscale grains. The GB sliding mechanism might hence contribute profoundly to the plastic deformation of NC Nb, which effectively led to enhanced strain rate sensitivity as shown in Fig. 6.

4.2.2. Regime of higher annealing temperature

After annealing at relatively high temperatures (200 to 400 °C), the strain rate sensitivity of NC Nb decreased slightly but was still much higher than that of as-deposited one (Fig. 6). Within this annealing regime (regime 2), the GB relaxation process proposed above for regime 1 should also be in operation. In this way, GB ledges were further eliminated while the intrinsic stress was persistently reduced, which should therefore result in even higher \( m \) compared with that derived from NC Nb annealed at 100 °C. However, such prediction contradicted the trend of \( m \) observed in regime 2 of Fig. 6. Alternatively, we next attempt to rationalize it by considering issues related to dislocations. The reduced density of mixed dislocations also contributed to the decreased of \( m \) according to Eqs. (6) and (7).

Despite the two aforementioned processes, GB relaxation occurred during annealing might affect strain rate sensitivity in another way. It was well known that dislocation-GB interaction was a high strain rate sensitivity process, as dislocations in nanoscale grains were nucleated from and annihilated at GBs [37]. Upon annealing, GB relaxation could effectively eliminate GB ledges as shown in Fig. 8, which were the main dislocation nucleation/annihilation sites [4,38], and hence could significantly reduce the strain rate sensitivity of annealed NC Nb. To evaluate the contribution of GB relaxation, the probability of a dislocation absorbed by GB could be described using the model of GB absorbed dislocations, as [39]:

\[ P_\text{dis} = \left[ 1 - (1 - p)^N \right]^J \]  

(8)

where \( N \) was the number of dislocation core atoms jumping into the GB during an average time absorption and was closely related to applied strain rate, and \( J \) was the total number of atoms of the dislocation core jumping into the GB and was dependent on grain size. Therefore, the values of \( N \) and \( J \) should be identical for fixed grain size and applied strain rate. Alternatively, \( p \) was the probability of an atom jumping into the GB successfully at one attempt, which was related to the structure of GB. In general, \( p \) was given by [39]:

\[ p = \exp\left( - (\Delta G + b^2 \Delta t)/kT \right) \]

where \( \Delta G \) was the activation energy of atomic migration, with ordered GB exhibiting lower \( \Delta G \). According to Eq. (8), \( P_\text{dis} \) should decrease for NC Nb annealed at relatively high temperature, causing more dislocation pile ups at GBs and therefore decreased strain rate sensitivity.

Above all, three processes, i.e., enhanced GB sliding, reduced dislocation density (involving dislocation structural evolution) and eliminated dislocation nucleation/annihilation sites, might operate simultaneously upon annealing for the present NC Nb. The three processes contributed to the strain rate sensitivity of NC Nb in different ways, as the first one enhanced while the second one first enhanced (due to the dislocation structural evolution) and then decreased the \( m \) (due to the mixed dislocation density), and the last weakened the sensitivity. Based on the experimental results of Fig. 6, in regime 2, one might expect that the attribution derived from enhanced GB sliding was compensated by the two other processes that contributed negatively to \( m \). Therefore, the value of \( m \) monotonically decreased as the annealing temperature was increased from 200 to 400 °C.

5. Conclusion

The unusual effects of annealing temperature on the hardness \( H \) and
strain rate sensitivity $m$ of NC Nb were evaluated experimentally. Two annealing temperature regimes were identified, in which $H$ and $m$ exhibited remarkably different variation trends upon annealing. For the former, strengthening occurred at elevated temperatures (above 200 °C), and two competitive mechanisms related separately to GB relaxation and reduction of dislocation density were proposed to dominate the two regimes alternatively. For the latter, annealing induced microstructural evolution, e.g., number of grain boundary ledges, densities of edge and mixed dislocations and dislocation nucleation/annihilation sites, was proposed to play a key role in determining the extent of strain rate sensitivity.

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References