Negative strain rate sensitivity in ultrahigh-strength nanocrystalline tantalum

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Nanocrystalline tantalum prepared through direct current magnetron sputtering exhibits a negative strain rate sensitivity behavior under nanoindentation; i.e., the hardness value of nanocrystalline tantalum decreases with increasing indentation loading rates. High resolution transmission electron microscopy reveals a beta- to alpha-phase transformation underneath the indents, suggesting that the pseudohexagonal to body-centered cubic structural transformation in nanocrystalline tantalum is likely pressure induced. Evidence of shear banding was documented along the edge of indents, consistent with the negative strain rate sensitivity observed. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2338006]

The strain rate sensitivity (SRS) of solid materials, commonly defined as $m=\partial \ln \sigma / \partial \ln \dot{\varepsilon}$ (where σ is the flow stress and $\dot{\varepsilon}$ is the strain rate), has important implications in understanding the mechanical behavior and deformation mechanisms of nanocrystalline materials.[1] Some unique deformation behaviors observed in nanocrystalline metals are often associated with an elevation or reduction of SRS compared with their coarse-grained counterparts.[2] For example, the near perfect elasto-plastic behavior reported in tensile deformation of nanocrystalline copper can be understood in terms of a three- to fourfold increase of m value at low strain rates ($\sim 5\times 10^{-6}$ s^{-1}).[3,4] In contrast, powder-consolidated nanostructured iron, albeit exhibiting a near perfect elasto-plastic behavior in compression, fails in shear banding mode due to diminishing strain hardening and reduced strain rate sensitivity.[5,6]

In the extreme case, negative strain rate sensitivity (NSRS) can occur in some nanostructured and conventional aluminum alloys.[7] Such NSRS is believed to be caused by a small scale phenomenon (known as Portevin-LeChatelier phenomenon) associated with interactions between dislocations and solutes.[8] For a pure nanocrystalline metal such as tantalum, no Portevin-LeChatelier effect is possible and thus the negative strain rate sensitivity is not normally anticipated. Here we report that physical vapor deposited nanocrystalline tantalum exhibits a negative strain rate sensitivity behavior under nanoindentations over a range of loading rates, from 50 to 50 000 μN/s. The origin of such NSRS behavior is examined.

High purity (99.95%) nanocrystalline Ta was fabricated by direct current magnetron sputtering onto a silicon (100) substrate (10 cm diameter) with a native dioxide layer. The sputtering gas was 99.999% pure argon and the deposition rate was 5 Å/s. Four nanocrystalline tantalum samples, with sputtering working pressure of 4.5–9 mTorr, were prepared through continuous deposition. The substrate temperature was monitored to be 27 °C during sputtering. The working pressure and substrate temperature are known to influence the residual stress of the deposited films and their microstructures.[9]

The residual stresses of the films were measured using a Tencor FLX-2320 thin film stress measurement instrument. The phase and microstructure of nanocrystalline Ta were examined by means of x-ray diffraction (XRD) and transmission electron microscopy (TEM), respectively. XRD was carried out on a Philips X'Pert Pro MPD x-ray diffractometer using Cu $K\alpha$ radiation at an acceleration voltage of 45 kV and a current of 40 mA. A Philips CM-300 FEG TEM operated at 300 kV was used to determine grain sizes and identify deformation debris in the samples. Table I is a list of as-synthesized nanocrystalline tantalum samples subjected to nanoindentation experiments. Due to low mobility of tantalum adatoms at room temperature, large compressive residual stresses were developed in the films, which increased with decreasing argon sputtering pressures. This trend is consistent with other results documented in the literature.[9]

It was determined from XRD, Fig. 1(a), that all the as-synthesized nanocrystalline tantalum samples have predominant tetragonal structure β-phase with zero or a negligible amount of body-centered cubic (bcc) α-phase. In addition, the films have a strong {002} fiber texture. Extensive plan-view TEM examinations suggest that all four Ta films have similar small grain sizes, in the range of 5–15 nm, and follow a narrow grain size distribution. The mean grain size, for example, measured for sample 4 shown in Fig. 1(b) is 9 nm. A slightly elongated grain structure is expected along the cross section as this is a typical microstructural feature of many nanostructured metals prepared by physical vapor deposition or electrodeposition.[1,10]

TABLE I. List of as-sputtered nanocrystalline Ta samples subjected to nanoindentation experiments and their corresponding hardness values measured with loading rates in the range of 50–50 000 μN/s.

Sample	Working pressure (mTorr)	Film thickness (μm)	Residual stress (MPa)	Dominant phase	Hardness (GPa)
1	3.0	1.5	−905	Beta	16–23
2	6.0	1.5	−841	Beta	16–21
3	7.5	1.89	−641	Beta	17–21
4	9.0	1.82	−456	Beta	17–21

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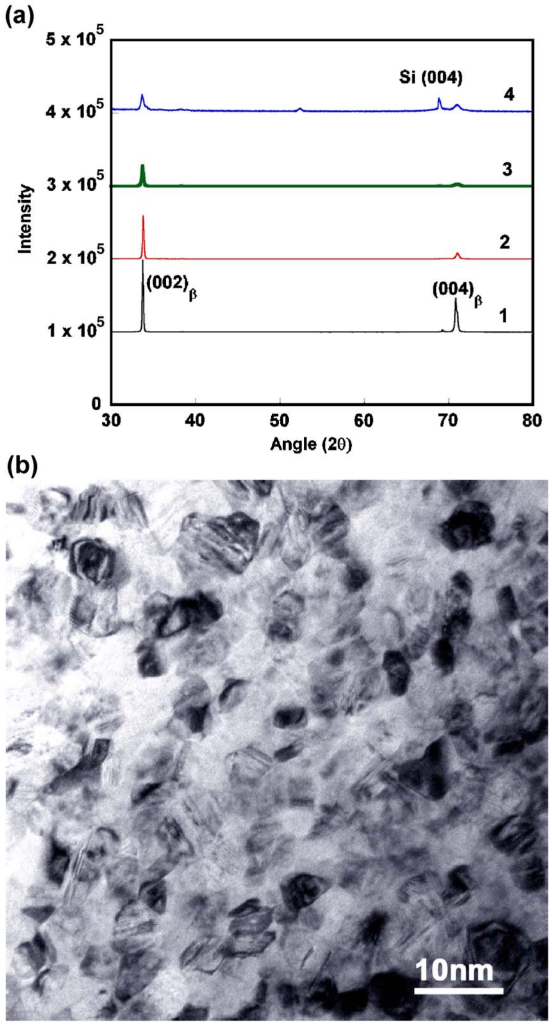

FIG. 1. (a) (Color online) X-ray diffraction patterns of as-sputtered β-Ta film. (b) Plan-view TEM micrograph of nanocrystalline Ta (sample 4 in Table I), showing a narrow grain size distribution.

The hardness values of nanocrystalline tantalum samples were measured using a TriboIndenter (Hysitron, Minneapolis, MN) at constant loading rates from 50 to 50 000 μN/s with a maximum load of 3600 μN. The indentation depth for all the measurements is 0.07–0.1 μm, which is less than one-tenth of the film thickness. A minimum of 20 indents were made at each indentation rate in order to obtain the reported hardness values shown in Table I and Fig. 2. The standard nanoindentation drift correction software was applied during all tests in order to correct any drift effects in the load versus displacement curves. The drift rate correction obtained for the slowest loading rate of 50 μN/s is 0.080 nm/s and becomes smaller as the loading rate increases. All the hardness values reported here are corrected with indentation drifts and have the standard deviation of less than 5%.

Despite slight differences in deposition conditions, the hardness values of all four nanocrystalline tantalum samples are in the range of 16–23 GPa, which is in line with the hardness value of beta-phase tantalum but much higher than that of alpha nanocrystalline tantalum (11.6 GPa).[11] The as-synthesized nanocrystalline tantalum is also three to four times stronger than that of similar grain-sized nanocrystalline Ni.[10,12] This highlights the importance of developing bcc or other crystal structured nanocrystalline metals for high strength applications.

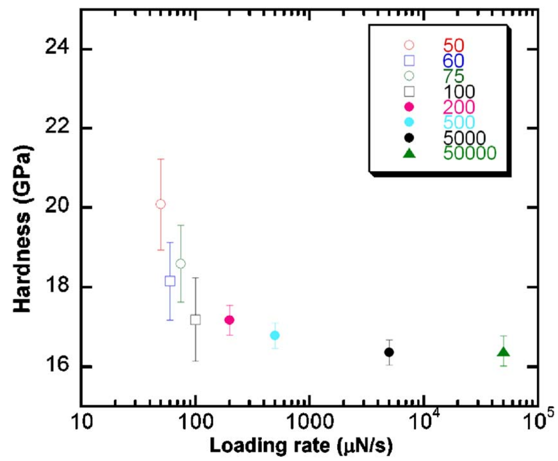

FIG. 2. (Color online) Hardness of nanocrystalline β-Ta as a function of indentation loading rate. A negative strain rate sensitivity behavior is observed (see text for details).

To investigate the strain rate dependent behavior of nanocrystalline Ta, Fig. 2 displays the hardness value of sample 4 as a function of indentation loading rate. Along with high strength, the hardness of nanocrystalline tantalum is observed to decrease with increasing loading rate. This phenomenon is true for all four samples and indicates a negative strain rate sensitivity behavior in nanocrystalline β-Ta. The result is counterintuitive to the experimental observations in other nanocrystalline pure metals, where only positive strain rate sensitivity has been documented so far.[2]

To examine the origin of such negative strain rate sensitivity behavior in nanocrystalline tantalum, we adopted the focused ion beam (FIB) technique (using FEI Nova 600 Dual-Beam FIB) to prepare cross-sectional TEM samples underneath the nanoindents, as shown in Fig. 3. The samples were cut such that the electron beam direction of the microscope is perpendicular to the film normal. Before ion-beam thinning, the contour of the indent was protected by platinum coatings and remains visible in the image [Fig. 3(c)]. High resolution TEM examinations show that the as-deposited β-Ta has a preferred {002} texture with line fringes of (002) plane oriented nearly parallel to the interface with the plane spacing[13] of 0.229 nm [Fig. 3(a)]. The fast Fourier transformation (FFT) pattern of the as-deposited structure shown in Fig. 3(b) reveals a distorted lattice structure without any high-fold symmetry (note that the electron beam direction is not necessarily parallel to the [001] zone axis). After indentation, TEM tilting experiments reveal some declined line fringes against the substrate near the indent [Fig. 3(d)]. The d spacing of these inclined lines is measured to be 0.236 nm. The inset FFT pattern taken from these inclined lines exhibits a sixfold symmetry, which is in distinguished difference from the as-deposited β-phase FFT pattern [shown in Fig. 3(b)]. We therefore relate these fringes to (110) α-Ta (d =0.234 nm). Our extensive TEM examinations of the area far from the indent reveal similar FFT pattern shown in Fig. 3(b) without any sixfold symmetry. This is an indication that beta- to alpha-phase transformation has occurred underneath the indents, leading to reduced hardness values.

Though it is a question of debate, some recent experiments inferred that deformation twinning could also lead to

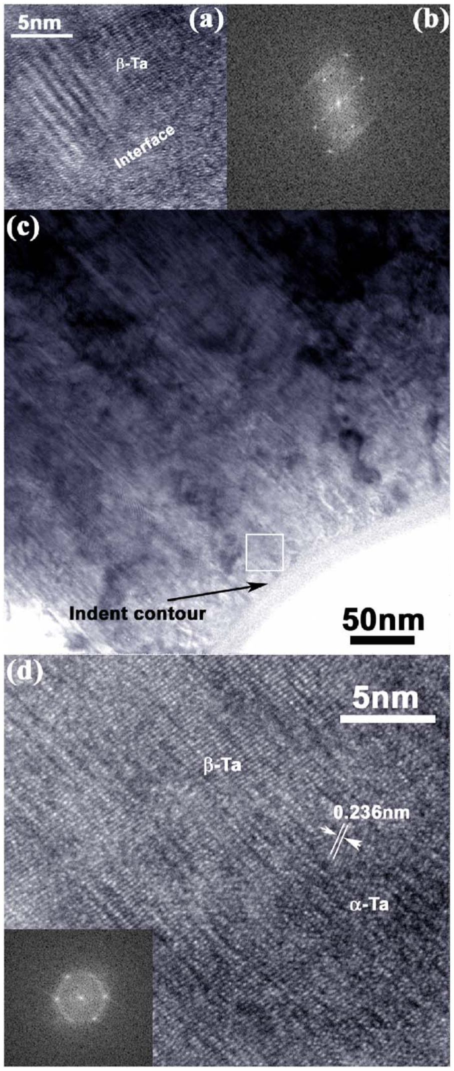

FIG. 3. (Color online) (a) High resolution TEM image of the as-sputtered β-phase nanocrystalline Ta, which has a preferred {002} fiber texture with (002) planes parallel to the interface (amorphouslike region). (b) Fast Fourier transformation (FFT) pattern of as-deposited β-Ta before nanoindentation. (c) A cross-sectional TEM image of a nanoindent at loading rate of 5000 μN/s. (d) High resolution TEM micrograph of the white frame area in (a), revealing formation of α-Ta underneath the indent. The inset is FFT pattern from the area in (b) marked with "α-Ta." The FFT pattern from the region far from the indent shows similar feature to the one shown in (b).

negative strain rate sensitivity in nanocrystalline metals such as cobalt.[14] Our TEM examinations excluded this possibility, as twinning activities were not found in β-Ta, which is very different from the twinning phenomenon observed in bcc nanocrystalline Ta during nanoindentation processes.[15] The phase-transformation-induced negative strain rate sensitivity reported here is commensurate to the fact that the NSRS behavior only occurs in β-Ta but not in α-Ta, where a normal rate dependent behavior was observed.[15] Our nanoindentation experiments at different loading rates also suggest that a higher indentation rate generally corresponds to a larger volume fraction of α-Ta in the deformed materials. This is consistent with the NSRS behavior discussed above.

Materials with negative strain rate sensitivity; i.e., the hardness/strength value decreases as the external loading (strain) rate increases, are prone to plastic flow localization in the form of shear banding. This has indeed been seen in nanocrystalline β-Ta. Figure 4 shows a scanning electron microscopy (SEM) image of an indent after deformation at a strain rate of 0.1 s^{-1} to a depth of $\sim$1 μm, using a MTS XP NanoIndenter. The shear localizations are clearly visible along the edge of the indent, similar to the shear banding observed in amorphous metallic glasses or certain multilayer metallic thin films.[16] The shear localizations appear to become more pronounced with increasing indentation loading rates. At the slowest indentation rate studied (0.025 s^{-1}), no shear banding was observed. This experimental evidence agrees well with the NSRS behavior observed above. The ultrahigh strength of beta-phase nanocrystalline tantalum and its negative strain rate sensitivity behavior suggest that β-Ta has potential applications as kinetic energy penetrators and explosive fragmentations.

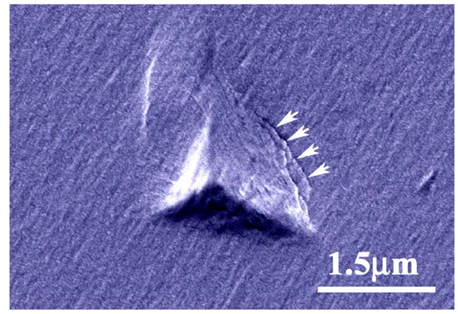

FIG. 4. (Color online) SEM image of an indent at the loading rate of 0.1 s^{-1} to a depth of $\sim$1 μm. Note that this indent was performed for testing shear localization only (not for hardness measurements). Shear banding (pointed with white arrows) can be seen along the edge of the indent.

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