pCorrelations between microstructure, fracture morphology, and fracture toughness of nanocrystalline Ni-W alloys

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Abstract: Ni-23at%W thin films were ion-beam machined and tested in bending. Microstructures were characterized with aberration-corrected electron microscopy and the fracture surfaces were inspected after each test with SEM. Nominally amorphous films fractured along oxide streaks that formed during deposition. Heat treating at 700 °C crystallized the samples to a grain size of 30 nm, and the corresponding fracture toughness increased from 2.1 to 2.5 MPa $\sqrt{m}$. This work demonstrates that mesoscale features and impurities influence amorphous and nanocrystalline Ni-W fracture.

Keywords: Nanocrystalline; Cantilever Beam Test; Fracture Toughness; STEM HAADF; Mesoscale Structures

Nanocrystalline metals formed from alloys such as Ni-W often offer attractive mechanical properties such as high hardness, but high strength is frequently accompanied by poor fracture toughness [1]. Unfortunately, reliable toughness information is limited because the small number of publications that report on the fracture of nanocrystalline metals indicate (1) that quantitative toughness measurements are challenging to conduct [2], and (2) that the toughness and fracture morphology may be functions not only of composition, pore size, and grain size, but also of mesoscopic features such as nanograin colony size [3]. Quantitatively determining fracture toughness of nanocrystalline metals remains a particular challenge because many such materials are thin films [4,5]. Conventional macro-scale tensile tests or hardness indentation measurements are generally neither feasible nor effective [6]. Likewise, analysis of structure and chemistry at a level sufficient to provide a complete description of the fracture process may require specialized characterization tools that are not widely available. As a result, very few studies have successfully conducted quantitative fracture toughness evaluation with detailed analysis of the links between toughness, microstructure, nanostructure, and localized chemistry.

Micro-scale cantilever beam testing provides one viable approach to quantitative toughness measurement [7,8]. It allows the isolation of a nanocrystalline thin film from its substrate and the selection of small defect-free regions to avoid large cracks or pores. In addition, proper selection of specimen preparation and testing conditions allows the use of linear

elastic fracture mechanics to determine accurate fracture toughness values. The approach has been successfully used to analyze a variety of material systems including single crystals [9–12] and bicrystal interfaces [13–16]. The fracture toughness of nanocrystalline Ni-W alloys with ~13 at.%W has also been successfully measured using notched micro-cantilever beam testing [17,18]. These experiments utilized LIGA-fabricated thin films that had a crystalline columnar microstructure with a column width of ~100 nm as determined using SEM and intercolumnar clusters of 20 nm grains as determined by X-ray diffraction. Nanoscale porosity was also present. The cantilevers were approximately 25 μm wide, 12 μm thick, and 40 μm long, with notch depths approximately 10% of the beam thickness. K_{IC} values ranged between 1.49 and 5.14 $\text{MPa}\sqrt{\text{m}}$; the large scatter was attributed to sample porosity. The fracture surfaces were examined using SEM but no direct correlation between the underlying microstructure and the crack path was reported.

The link between fracture morphology and micro/nanostructure of Ni-W was the focus of a different study in which nanocrystalline films ranging from approximately 13 to 22.5 at.%W were bent in tension while still attached to the underlying metal substrate [3]. It was found that the 5-20 nm nanocrystalline grains were organized into columnar colonies 3-5 μm in width. The crack path tended to follow the inter-colony boundaries of the films electrodeposited under direct current and pulsed current conditions. For those films, distinct inter-colony surface grooves were observed and significant W enrichment was measured on the sub-surface inter-colony boundaries using Auger spectroscopy. Films deposited using reverse-pulsed current also showed surface grooves indicating underlying colonies, but there was little W enrichment and little tendency of the crack path to follow the interfaces; instead, the fracture surface was relatively flat. No quantitative fracture toughness measurements were performed so it is not known if the changes in fracture morphology correspond to significant differences in toughness.

In the present study, electrodeposited Ni-23 at.%W alloys were studied using a combination of in-situ micro-scale cantilever beam deflection tests within a scanning electron microscope (SEM) and scanning transmission electron microscopy (STEM) characterization to relate changes in microstructure to fracture behavior. Some of the films were heat treated to alter the microstructure without altering the average composition.

Ni-23 at.%W alloys were electrodeposited onto commercially pure Cu and Ni substrates using reverse-pulsed current methods developed by Detor [19] and a bath composition formulated by Yamasaki [20]. The forward current density was 0.2 A/cm^2 applied for 20 ms, followed by a reverse current density of 0.1 A/cm^2 applied for 3 ms. Several specimens were heat-treated at 300 $^{\circ}\text{C}$ or 700 $^{\circ}\text{C}$ for four hours in a horizontal tube furnace with flowing Ar + 5 mol.%H₂. TEM samples were extracted from as-deposited and heat treated specimens and thinned using a FEI DB-235 focused ion beam (FIB), followed by cleaning with a Fischione NanoMill 1040. Diffraction patterns were collected with a JEOL JEM-2000FX TEM and STEM micrographs were recorded with a JEOL JEM-ARM200CF aberration corrected STEM.

Cantilever beams for fracture testing were fabricated by FIB milling. The beam dimensions were nominally 3 μm $\times$ 3 μm $\times$ 15 μm ; the actual dimensions of every beam were measured pre- and post-fracture in the SEM. A pre-crack notch nominally 1.2 μm deep (40% of the beam thickness) was ion milled on the top surface of each beam, extending across the center

of the cantilever but leaving intact bridges ~100-200 nm wide on both ends to avoid uneven milling at the beam edges [12,15,21]. Fracture toughness and conventional cross-section nano-indentation tests were conducted in the SEM with an in-situ Hysitron PI-85 Picoindenter. This instrument has a maximum load capacity of 10 mN, and load and displacement resolution on the order of 1 μ N and 5 nm, respectively. Toughness measurements used a constant loading rate of 5 μ N/s. The fracture toughness K_{IC} was calculated following a procedure described previously [15] using the equations established by Koyama [10]:

$$K_{IC} = \frac{6FL}{W^2 B} \sqrt{\pi a} \cdot f(a/W) \quad (1)$$

$$f(a/W)_{isotropic} = 1.122 - 1.40(a/W) + 7.33(a/W)^2 - 13.08(a/W)^3 + 14.0(a/W)^4 \quad (2)$$

where F is the fracture load, L is the distance between the notch and the loading point, W is the thickness of the beam, B is the width of the beam, and a is the notch depth. An analysis of the uncertainties in the individual quantities leads to an estimate of the uncertainty for the calculated value of K_{IC} of less than 10%.

Fracture surfaces were imaged using a Carl Zeiss Leo 1550 Scanning Electron Microscopy (SEM). The hardness measurements were performed on film cross-sections using a diamond cube corner indenter and loads up to 3150 μ N to maintain an indentation depth of 200nm. Hardness values were determined by the Oliver-Pharr method [22].

Typical high-angle annular dark field (STEM-HAADF) STEM micrographs with selected area diffraction pattern (SADP) insets are shown in Figure 1. The as-deposited (AD) and 300 °C samples were nominally amorphous, in agreement with the SADP diffuse diffraction rings. The same samples exhibited growth layers in the TEM, indicated by the contrast variations parallel to the substrate in Figures 1a and 1b, and 100-200 nm wide columnar micro-domains as indicated by sudden changes in growth layer curvature. The 700 °C specimen was fully crystalline and comprised of 30 nm grains. Several phases including Ni(W) solid solution, Ni₄W, Ni₆W₆C, and nanoscale tungsten oxide (WO_x) were detected. The bright phases seen in Figure 1c correspond to Ni₆W₆C, and the small dark phases are WO_x. The presence and identification of the carbides has been discussed previously [23]. No pores were found in the TEM specimens. The surfaces of the films were examined using SEM. Scattered pores were observed but there were no deep grooves correlating to the subsurface structure.

Figure 1. STEM-HAADF images and SADP of (a) as-deposited, (b) 300°C, and (c) 700°C heat treated specimens.

Representative load-displacement data are shown in Figure 2a. All specimens exhibited linear elastic behavior with abrupt changes in slope corresponding to side-bridge cracking prior to catastrophic failure. Finite element simulation of cantilever beam stiffness with and without side bridges confirmed that the observed slope changes were consistent with full cracking of the bridge ligaments. The tests were observed in the SEM as they occurred; sidewall cracks corresponding to failure of the side bridges were visible prior to catastrophic failure but no evidence of plasticity or gradual cracking in the region below each notch was evident. The corresponding fracture toughness results are shown in Figure 2b. Each result represents either 3

or 4 measurements. The average values of toughness are 2.15 ± 0.08 (as-deposited), 1.96 ± 0.08 (300 °C), and 2.52 ± 0.10 (700 °C) MPa $\sqrt{\text{m}}$. The error bars represent 95% confidence. The spread between individual toughness measurements for each specimen condition is relatively small compared to the scatter in previous reports [17,18]. This is likely due to the use of small beams that avoided large internal flaws and to the deep pre-crack notches. Our experience with shallower notches that fail to satisfy the ASTM standard requirement for crack size during plane strain fracture toughness testing [ASTM E399] is that they lead to greatly increased scatter. Annealing of the films at 300 °C led to a small decrease in fracture toughness despite the increase in strength (i.e., nanoindentation hardness) seen in Figure 2c. Student's t test revealed that the decrease in K_{IC} due to annealing is statistically significant. Annealing at 700 °C led to a statistically significant increase in K_{IC} , presumably because of the large increase in strength associated with the development of the nanocrystalline structure.

The absolute values of K_{IC} shown in Figure 2b must be considered as upper bounds for the actual values due to the error associated with the bluntness of the ion-milled notch tip. An expression quantifying the influence of the notch radius on the apparent fracture toughness of polycrystalline materials was proposed by Gomez et al. [24] for Single Edge V-Notched Beam (SEVNB) specimens. This relationship can be written as:

$$K_a = K_{IC} \sqrt{1 + \frac{R}{8r_c}} \quad (3)$$

where K_a is the apparent fracture toughness values measured by the test, K_{IC} is the real fracture toughness value, R is the notch radius, and r_c is a critical distance which is equal to the grain size. In this study, the typical notch radius created by the FIB was determined to be about 12 nm. The average grain size of the 700 °C heat treated Ni-W nanocrystalline samples was determined to be approximately 30 nm. The ratio of K_a/K_{IC} is determined by equation (3) to be 1.03 for the 700 °C heat treated samples. This indicates that the error associated with the crack tip curvature is only about 3%.

Figure 2. Comparisons of (a) representative load-displacement behavior, (b) fracture toughness, and (c) hardness among all three samples.

Figure 3 shows low magnification SEM images of the cantilever beam test configuration immediately before and after fracture, and also shows representative fracture surfaces of the AD, 300 °C, and 700 °C samples. The AD surface exhibited 200 nm wide undulating ridges running vertically along the beam cross-section with matching convex and concave ridges on alternating sides, despite having initiated from a linear pre-crack. The 300 °C fracture surface still exhibited vertical matching features, although the scale of the features was reduced. Top-down views of the AD and 300 °C fracture surfaces are shown in Figures 4a and 4b, respectively. In comparison to the AD specimen, the vertical features of the 300 °C sample are less pronounced and the surface appears more uniform. Considering that both the AD and 300 °C samples were mostly amorphous, it might be expected that the fracture surfaces would be similar but this was not the case. To investigate further, high magnification STEM-HAADF images were recorded as shown in Figures 4a and 4b. Both samples displayed oxide streaks, confirmed with X-ray energy

dispersive spectroscopy (STEM-EDS), along the columnar domain interfaces. However, the oxide streaks found in the AD specimen were spaced approximately 200 nm apart, well-defined, continuous, and aligned in the direction perpendicular to the film surface, whereas the streaks found in the 300 °C specimen were closer together, less defined, and branched. Thus, we conclude that the undulating morphology of the AD sample is due to the crack following weak inter-columnar vertical oxide trails, and the more uniform fracture surface of the 300 °C specimen is due to the more closely-spaced, discontinuous nature of the branched oxides. Further supporting the supposition that the oxide streaks determined the fracture path, the widths of the fracture surface features generally match the domain widths seen in Figures 1a and 1b.

Figure 3. Cantilever beam test configuration immediately (a) before and (b) after fracture, and fracture surfaces of (c,f) as-deposited, (d,g) 300°C and (e,h) 700°C beams. Images in (c-e) show the fracture surfaces of the beam sections that are still attached to the bulk material and images in (f-h) show the surfaces detached from the bulk material.

Figure 4. STEM-HAADF images of the oxide streaks found in the (a) as-deposited and (b) 300°C samples.

The lower fracture toughness of the 300 °C specimens is somewhat surprising given the intermediate indentation hardness. However, it is important to note that a strength measurement performed in compression may not relate to the conditions that lead to fracture in tension. Furthermore, the reduced fracture toughness of the 300 °C specimen relative to that of the AD specimen is consistent with the decreased fracture surface area. Thus the combination of in-situ quantitative toughness measurements combined with observation of the fracture surfaces provides greater insight than either approach performed in isolation.

In contrast with the amorphous specimens, the 700 °C fracture surface exhibited an intergranular fracture path which may contribute to the increase of the fracture toughness. The feature size on the surface matches well with the average grain size of 30 nm. The 200 nm Ni₆W₆C particles did not influence the fracture path in any noticeable fashion.

Consistent fracture toughness measurements with low scatter of data of as-deposited and heat treated nanocrystalline Ni-W thin films were obtained by a micro-cantilever beam deflection test. All samples failed in a brittle manner, and the 700 °C heat treated specimen exhibited the highest fracture toughness of $2.5 \text{ MPa}\sqrt{\text{m}}$. The fracture surfaces differed between all three specimens. Oxide streaks located on columnar domain interfaces were found to influence the fracture paths of the nominally amorphous films, whereas the crystalline film experienced intergranular failure. It suggests that the annealing of the as-prepared Ni-W thin films at higher temperatures does not change fracture toughness in a simple way: the changes depend on the nature of fine-scale microstructure and impurities in the Ni-W alloy. Furthermore, because the morphology of the oxide streaks is responsible for the distinctive fracture paths observed in each of the amorphous films, the influence of mesoscale features is not limited to the case of columnar nanocrystalline grain colonies observed previously.

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fig 2

In-situ Bend Testing

**Amorphous
Ni-W**

**Nanocrystalline
Ni-W**

Mesocale
Columnar Domains

Impurity
Oxide Streaks

Jagged
Fracture Surfaces

Multi-Phase
Microstructure

Impurity
Oxide Particles

Intergranular
Fracture Surfaces