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Influence of grain size on the strength size dependence exhibited by sub-micron scale nickel structures with complex cross-sectional geometries

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ABSTRACT

Sub-micron scale columnar nickel structures with different cross-sectional geometries and grain sizes were successfully fabricated via electron beam lithography and electroplating methods. Uniaxial microcompression tests revealed the flow stresses of these structures increase with smaller grain sizes, in close agreement with the Hall-Petch relationship. Size dependent softening effects were only observed in nickel pillars with average grain sizes in the range of 9.4–13.2 nm. In contrast, pillars with grain size near ~22 nm do not exhibit any flow stress dependence on size, with the pillar strengths remaining relatively constant. In addition, for nickel pillars with the same microstructures, there is no observable dependence of flow stresses on the cross-sectional geometries.

1. Introduction

Bulk nanocrystalline metals, with grains smaller than 100 nm, are often much stronger than their coarser grain counterparts, a strengthening mechanism commonly known as the Hall–Petch effect [1,2]. However, a wide body of mechanical characterization results from sub-micron scale columnar structures of nanocrystalline platinum [3], nickel–tungsten alloy [4], bismuth [5], and cobalt [6] show the strengths of these small features may also depend on the critical external dimensions of the structure. For example, Gu et al. [3] demonstrated that the mechanical strengths of small scale nanocrystalline platinum pillars with an average grain size near ~12 nm reduce with column diameter. Their molecular dynamic simulations attributed this softening phenomenon to the increased contribution of grain boundary mediated deformation near the specimen surfaces. Grain boundary mediated contributions to pillar plastic deformation continues to increase as the ratio between pillar diameter and grain size reduces. Gu et al. [3] observed that nanocrystalline platinum pillars soften when the diameters are approximately five times the grain size. Burek et al. [5] also observed similar weakening of bismuth sub-micron columnar scale when the sample microstructures change from single-crystalline to polycrystalline, with the reduction in mechanical strength of the polycrystalline specimens due to emerging grain boundary mediated deformation. Wu et al. [7] used large-scale molecular dynamics simulations to understand the deformation mechanisms operating in small scale nanocrystalline nickel pillars under uniaxial tension, with their results indicating an increase of grain boundary sliding activities as the ratio between the pillar diameter and the grain size reduces.

However, recent work performed by Rinaldi et al. [8] reveals an opposite effect, where sub-micron scale nanocrystalline nickel columns with a mean grain size of ~30 nm, machined to columns using focused ion beam (FIB) milling techniques, become stronger with the reduction of pillar diameter. This is in contrast with previous works reported by Jang and Greer [4] on Ni–4.4%W alloy pillars, where specimens softened with reducing pillar dimensions. It is unclear if the tungsten alloying contributed to the different size dependences.

The objective of this work was to shed further light on the deformation mechanisms of nanocrystalline metals – specifically nanocrystalline nickel (nc-nickel) – at the sub-micron scale, which ultimately will help interpret inconsistencies reported in prior works [4,8] on the strength size effect in similar structures. In addition, the effects of average grain size on the softening

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effects were studied by maintaining the same pillar geometries, while varying the grain sizes in the range of ~9.4 and ~22.7 nm. Nickel is a face-centered-cubic metal with wide industrial applications because of its high mechanical strength and ductility. Bulk scale nc-nickel has been fabricated and well characterized by other researchers [9–16]. This material has a Hall–Petch slope in the range 6.49–13.33 GPa/nm$^{-1/2}$ [14]. However, very few experimental studies have been conducted to understand the mechanical deformation behavior of sub-micron scale nc-nickel structures. Specimens prepared for this work are sub-micron scale nc-nickel columns with various complex cross-sectional geometries fabricated via electron beam lithography and electroplating methods. The fabricated columnar structures included solid core pillars with different diameters, c-shaped posts, hollow-shaped pillars, and x-shaped columns. This group of geometries was selected since they represent columnar structures with different surface areas to volume ratios in the range ~0.02 to ~0.004 nm^{-1}. Strength results collected from the various fabricated structures will help to understand how this geometric parameter influences the mechanical behavior of small scale nc-nickel pillars. Information on the effects of complex cross-sectional geometries on mechanical strengths for nanocrystalline materials is rare due to the difficulties in fabrication. Recently, Jahed et al [17] and Tsui et al. [18] characterized the compressive flow stresses of submicron scale cobalt and ruthenium pillars, and in both works significant influence of the pillar geometry on the measured flow stresses was not observed. Another important reason to examine the material strength of such shaped structures stems from the fact complex structures are commonly used in the micro/nano-electromechanical systems (MEMS/NEMS), nanoelectronics, and other practical small scale devices. Understanding the strengthening mechanisms of shaped sub-micron scale components is critical to device performance and reliability.

Results of uniaxial microcompression tests revealed the strengths of fabricated nc-nickel columns increased with smaller grain sizes. Since the amount of carbon and sulfur incorporated in the nickel matrix during electroplating was very small, solute strengthening contributions by these elements was deemed insignificant when compared with the amount of observed flow stress increases. Therefore, it is believed that the specimens with smaller grain sizes are strengthened by the Hall–Petch effect. In addition, results show not all of the specimens characterized exhibit size dependent softening effects – only nc-nickel columns with smaller average grain sizes exhibited a flow stress reduction with shrinking pillar diameter. Specimens with larger average grain sizes did not reveal any softening effects, even for pillars with diameter as small as 220 nm. In fact, the results may indicate that the smaller samples are slightly stronger. Finally, specimens with identical microstructures but with different complex cross-sectional geometries were observed to possess nearly identical mechanical strength characteristics.

2. Experimental

Sub-micron scale nickel columns were fabricated with specific microstructural control via electron beam lithography and electroplating methods, the details of which have been described previously [19]. Briefly, silicon substrates coated with thin titanium (~20 nm) and gold (~20–60 nm) layers were spin coated with polymethylmethacrylate (PMMA) resist prior to the electron beam exposure processes. Patterned PMMA molds consisted of via-holes with different cross-sectional geometries and were subsequently filled with nc-nickel by electroplating. The final microstructure of nc-nickel columns was tuned by the electroplating solution chemistry. The based electroplating solution contained fixed concentrations of nickel (II) sulfate hexahydrate (99%, Sigma Aldrich), nickel (II) chloride (98%, Sigma Aldrich), and boric acid (BX0865, EMD Millipore), as described in Table 1. From the base electroplating solution, two variations – named solution batch A and B – were created. Solution batch A contains the organic additive saccharin (98%, Sigma Aldrich) to yield nc-nickel pillars with smaller target grain sizes [20], while solution batch B is free of any grain size modifiers (i.e. the base solution).

Table 1
Nickel plating solution compositions for nanocrystalline nickel (g/l).

Solution batch	H_3BO_3 (g)	$NiCl_2 \cdot 6H_2O$ (g)	$NiSO_4 \cdot 6H_2O$ (g)	Saccharine (g)	Target grain size
A	30.0	30.0	300.0	1.9	Small
B	30.0	30.0	300.0	0.0	Large

Nickel pillars with different cross-sectional geometries were deposited on the same silicon substrate simultaneously in the same electroplating solution, and thus, were expected to possess nearly identical microstructures for each solution batch. All of the deposition processes were carried out at room temperature with a direct current density maintained at 11.5 ± 2 mA/cm^2. During electroplating, a commercially available pure nickel anode was used. Following nc-nickel electroplating, the PMMA mold was removed with acetone. Advantages of this fabrication process included strong sample uniformity across each substrate, and that any mechanical contact to nc-nickel pillars was avoided. Therefore, any defect generation on pillar surfaces which may produce premature yielding or fracture was minimized. The aspect ratios of the final pillars were in the range 1.0–1.5.

Uniaxial microcompression tests of fabricated nc-nickel pillars were performed with an in-situ nanoindenter (Nanomechanics Inc, Knoxville, TN) equipped with a customized 8 μm × 8 μm diamond square punch. The specimens were deformed at a nominal strain rate of 10^{-3} s^{-1}. All compression tests were carried out in a nitrogen purge environment under atmospheric pressure. Continuous stiffness measurement (CSM) hardware was not enabled during these experiments to eliminate uncertainties related to the displacement oscillation. A nanoindenter drift rate of 0.05 nm/s or smaller was set for all compression tests.

3. Results and discussions

Representative scanning electron microscope (SEM) images of as-fabricated nc-nickel columns are shown in Fig. 1. The micrographs display solid core pillars and columns with complex cross-sectional geometries, such as, hollow, c-shape, and x-shape. Solid core pillars with nominal diameters of 1000 nm and 220 nm are shown in Fig. 1(a) and (b), respectively. Other complex shaped structures, with ~1000 nm outer diameters, are shown in Fig. 1(c)–(e). Nc-nickel pillars displayed in Fig. 1, which were electroplated from solution batch A, exhibit smooth sidewalls and flat pillar tops. In addition, the pillar sidewalls are in nearly perfect vertical alignment with the substrate surface, with the exception of noticeable tapering near the base of the x-shaped structures. The micrographs also revealed slight off-centered placement of the cylindrical hole within the hollow pillars. Virtually identical geometrical characteristics were observed for nc-nickel prepared with the other solution batch, which is expected since all pillars were produced from identically processed PMMA molds. Detailed geometrical analysis of these sub-micron nc-nickel structures is summarized in Table 2. Two wall thickness values are reported to describe the hollow pillar geometries to properly describe the off-set placement of the central