

Fabrication, characterization and testing of thin films with novel microstructures

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A new approach is presented to produce uniform thickness, electron-transparent, free-standing single-phase or multiphase thin films with nanocrystalline grain sizes that lend themselves readily to in situ heating and straining in a transmission electron microscope. The second phase in the multiphase films is in the form of through-thickness rods, and their diameter, spacing and spatial arrangement can be controlled. Preliminary results of deformation studies on such films are presented.

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There appear to be two principal limitations in characterizing and mechanically testing materials with novel nanoscale multiphase microstructures. The first is the inability to produce them in bulk quantities and the second is the inability to perform in situ tests at high enough magnifications to track local changes in microstructure during deformation. The latter problem stems from the inability to perform in situ tests in the transmission electron microscope (TEM) on satisfactory quality specimens. Conventional methods to produce TEM specimens lead to non-uniform specimen thickness, often with a gradation from very thin electron transparent regions to thicker electron-opaque regions. Furthermore, multiphase materials etch differently leading to microstructure-biased thickness in the specimen. If mechanical tests or crack growth experiments are performed in the TEM on such specimens, the outcome can be easily biased by this non-uniformity. Free-standing thin film specimens have been created of pure metals or of microlaminates (two different materials) and successfully examined in the TEM [1–3]. However, studies on free-standing films containing a controlled dispersion of a second phase or a controlled dispersion of microstructure scale has not been published thus far to the best of our knowledge.

In this letter, we present (i) a novel approach to create free-standing thin films of nanoscale multiphase micro-

structures, (ii) a pathway that enables this microstructure to be changed and (iii) results of in situ testing such microstructures in the TEM. An added benefit of this processing route is the ability to control periodicity as well as the scale of the microstructure, which in turn can provide for direct verification of microstructure-based deformation models. We illustrate these aspects with two different case studies. The first consists of sub-micron pillars of nanocrystalline Cr embedded in a nanocrystalline Cu matrix in a periodic regular square array and the second consists of pillars of large-grained Cu embedded in a nanocrystalline Cu matrix. We illustrate how such films can be attached to a tensile template and tested in situ in the TEM, enabling documentation of crack propagation and crack interaction with the microstructure. Such an approach may provide detailed information on deformation response of such nanocrystalline materials at a mesoscopic scale and enable verification of several current hypotheses.

Our goal is to produce free-standing, uniform thickness, thin films of multiphase microstructure that are electron-transparent in conventional TEMs (~100 nm thick films). Furthermore, the intent is to mount these films on a straining device and enable them to be strained within the TEM so that a crack may be generated in the field of view that can then be followed to understand how it interacts with the microstructure ahead of it. It is envisioned that, by using other novel non-destructive characterization tools (e.g. non-contact atomic force microscopy), elastic properties of the film

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can be obtained and from there on, as a next step, one could estimate the fracture toughness of these multiphase nanostructural films using the in situ crack growth results in combination with computations. It is implicit that this approach and analysis would be representative of a material in a state of plane stress as the specimens being characterized are thin films.

We start with a cleaved surface of a single crystal of NaCl. A lithography approach is adopted to produce the multiphase film. Photoresist is first applied on the single crystal surface to a thickness of ~ 180 nm. Then a standard e-beam lithographic technique is used to produce a square array of perforations in the photoresist of predetermined spacing and perforation diameter. In this study, we have used a diameter of 500 nm and a spacing of 2 μm . Next, the assembly is transferred to an e-beam evaporator chamber and metal 1 (e.g. Cr) is deposited on the photoresist to a height of ~ 100 nm. The photoresist is then etched away leaving behind the metal pillars. Following this step, an option is available to either heat treat the free-standing nanocrystalline pillars to grow the grains or to leave the pillar grain size in the as-deposited state. The next step is to deposit metal 2 (e.g. Cu) to fill the space between the pillars. The deposition of metal 2 on top of the pillars will be eventually removed by ion milling. These film-preparation steps are illustrated schematically in Figure 1.

Grids, 3 mm square, are then cut on the deposited multiphase film using a scalpel, ensuring the depth of cut is adequate to reach the NaCl surface. The assembly is then introduced at an angle into water to enable the water to wick along the NaCl/film interface, liberating the film grids onto the water surface. A standard 3 mm TEM Cu grid with mesh openings of ~ 100 μm square is then used to lift the film grids after applying M-bond (a TEM compatible adhesive) to the Cu grid wires using a bench microscope. Care must be exercised to ensure the glue is only applied to the grid wires and does not span the open space between the wireframe. The assembly is allowed to dry for several hours. The free-standing film may now be examined in the TEM to characterize the microstructure, and if a heating stage

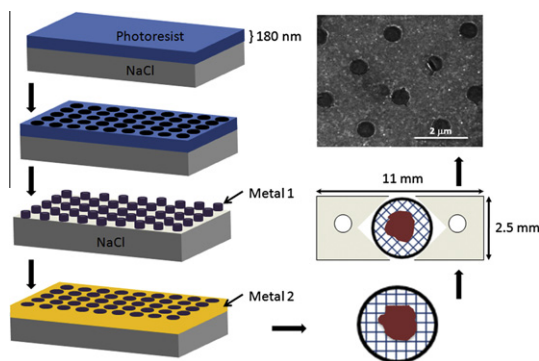


Figure 1. A schematic illustration of the steps to produce a two-phase “pillar” composite free-standing electron-transparent thin film that is then mounted on a stainless steel microtensile template. The last image in the sequence shows a low magnification TEM micrograph of a square array of nanocrystalline Cr pillars embedded in a nanocrystalline Cu film.

is available it can be heat treated in the TEM to modify the microstructure of the matrix and/or the pillar, as well as to modify (enhance) the matrix/pillar bonding. If metals 1 and 2 are reactive, the extent of interface reaction can be controlled/studied by varying the temperature and duration of exposure to temperature within the TEM. The final step involves attaching such a grid to a stainless steel sheet tensile template that is machined to fit the TEM straining stage with an additional hole (~ 2 mm) in the center of the template to enable the grid to be glued to it, so that the free-standing film can be viewed in a transmission mode. These sequential steps of TEM specimen preparation from the film as well as a representative micrograph of a square array of Cr pillars in a Cu matrix are also shown in Figure 1.

The microstructure of the as-deposited Cu matrix (Fig. 2a) confirms a nanostructured grain size with an average grain size of ~ 40 nm, although some regions in the foil (not explicitly visible in Fig. 2a) exhibited a grain size of around 10 nm. The Cr pillar likewise also exhibited a comparable nanostructure with a similar mean grain size (Fig. 2b). In situ annealing in the TEM was performed at various temperatures and representative micrographs after annealing at 600 $^{\circ}\text{C}$ are shown for the Cu matrix and the Cr pillars in Figure 2c and d. Significant grain growth has occurred in the Cu matrix with grain sizes in the range of 100–500 nm, whereas the Cr grain size remains virtually unchanged (compare Fig. 2b and d). In situ tension tests were conducted on both the as-deposited Cu–Cr composite and after the 600 $^{\circ}\text{C}$ anneal, and the results are shown in Figure 3a and b. In the as-deposited condition, the crack advances in the matrix Cu with minimal plasticity and when it approaches the Cr pillars it appears to prefer interface decohesion. Additionally, interface decohesion occurs along the main crack as well as in newly nucleated cracks ahead of the main crack, as seen in Figure 3a. In contrast, in the annealed condition, where the Cu grains are significantly larger, extensive plasticity and repeated crack blunting and resharping

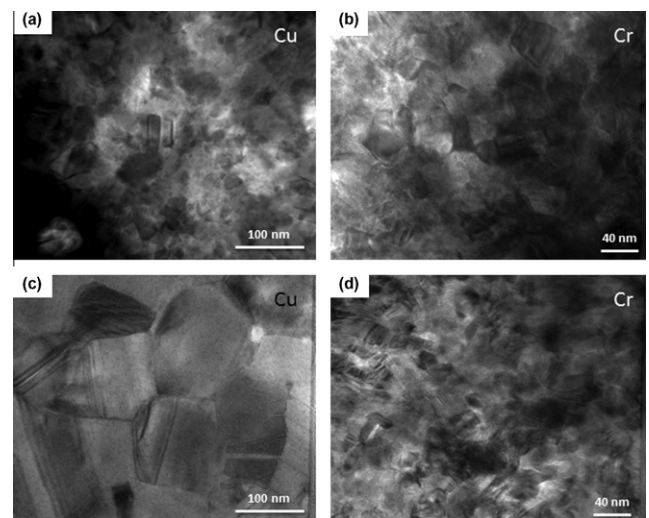


Figure 2. Electron microscopy images showing the nanocrystalline grain sizes in the as-deposited state in (a) the Cu matrix and (b) the Cr pillar. After annealing at 600 $^{\circ}\text{C}$, the Cu grains have grown significantly (c), whereas the Cr grains remain nanocrystalline in size (d).

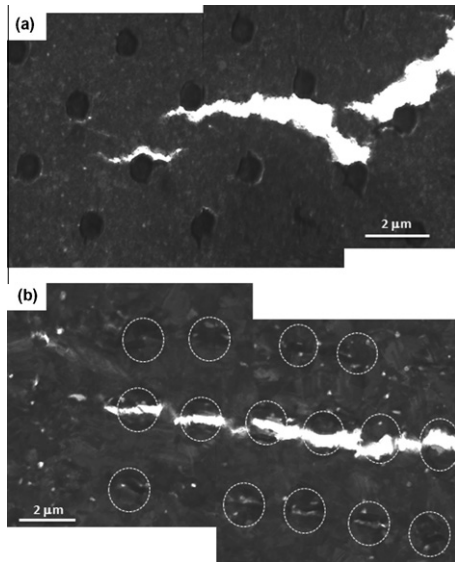


Figure 3. (a) Microstructure and damage in the crack-tip vicinity in the as-deposited Cu–Cr pillar composite thin film during in situ straining in the TEM. The crack appears to run along the Cu/Cr interface. (b) The crack goes through the pillars in the annealed structure. In both cases new cracks appear to nucleate ahead of the main crack and subsequently link with the main crack.

were observed as the means for crack growth. When the crack approached the Cr pillars, rather than circumventing them by traveling around the interface as previously observed, the crack splits the pillars repeatedly (Fig. 3b; here the dashed circles are used to train the eye on the pillars). Clearly, the annealing process is influential in affecting the grain size of the Cu, and also likely influences the interfacial bond strength. It is worth mentioning that one of the benefits of selecting the Cr–Cu system is that there are no interfacial reaction products/intermetallics in this

system; furthermore, the solubility of Cu in Cr (and Cr in Cu) is small, thereby protecting the integrity of the pillar geometry and the interface during the course of the anneal. Thus this novel approach enables the examination of the crack growth process, the sequence of failure events and the crack-tip deformation behavior at the mesoscopic scale in these uniform thickness films, and further demonstrates, by in situ heat treatment in the TEM, how it is possible to dramatically change the course of events.

We now use a second example to illustrate the versatility of this methodology. Here we have created another novel microstructure composed of a periodic array of large-grained Cu embedded in nanocrystalline Cu. The benefits of such microstructures have been discussed in the nanocrystalline material literature recently [4–6]. Specifically, a bimodal distribution of grain size in Cu and Ni has been shown to be advantageous in producing an optimal combination of high strength and reasonable ductility. Nanocrystalline metals with a narrow, unimodal grain size distribution have high strength but typically suffer from low ductility [7]. However, such bimodal grain sizes have typically been obtained by abnormal grain growth and controlling the distribution of these coarse grains has been a challenge; therefore, at a fundamental level, how these coarse grains specifically influence plastic deformation and fracture is not fully understood.

Different from the processing route described above for the Cu matrix–Cr pillar composite is the fact that we start with Cu pillars rather than Cr pillars and, after stripping the photoresist, the Cu pillars standing on the NaCl substrate is subjected to an anneal at 500 °C for 6 h in a vacuum furnace to grow the Cu grains in the pillars prior to depositing the second metal (also Cu in this case). Following this, TEM specimen preparation follows the steps previously outlined. This specimen is then strained in situ in the TEM with no further anneals in the TEM.

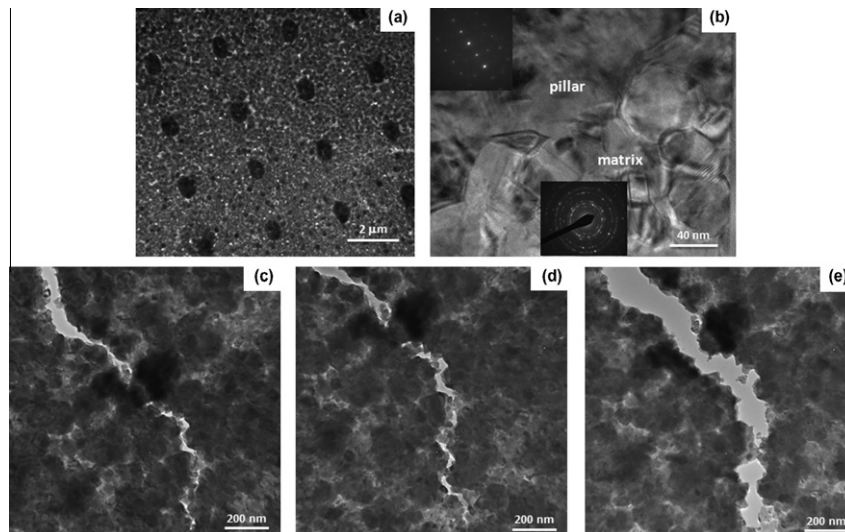


Figure 4. (a) A square array of microcrystalline Cu pillars embedded in a matrix of nanocrystalline Cu. (b) Cu pillar/Cu matrix interface showing interface integrity, the large grain size in the pillar and the associated selected area diffraction spot pattern, and the nanocrystalline grain size in the Cu matrix and the associated selected area diffraction ring pattern. (c, d and e) A sequence of images showing a matrix crack being bridged by a coarse Cu grain, the grain being plastically deformed and fractured while it shields the matrix crack tip and eventually the coarse Cu grain ruptures, causing the main crack to propagate unstably in the matrix.

A low magnification TEM image (Fig. 4a) shows the periodic square array of coarse-grained Cu pillars embedded in a nanocrystalline Cu matrix. A higher magnification image of the interface region (Fig. 4b) confirms (i) a continuous interface with no visible oxides or other impurity particles, (ii) nanocrystalline Cu grains constituting the matrix (40–50 nm grain size) and providing a diffraction ring pattern, and (iii) coarse-grained Cu within the pillar with an associated diffraction spot pattern, as would be expected. Crack growth behavior in this microstructure is captured in a sequence of time-lapse images where the coarse-grained Cu pillar is seen to bridge an otherwise rapidly growing crack in the relatively brittle matrix (Fig. 4c) and, with further loading, experiences plastic deformation and tearing (Fig. 4d) before eventually parting completely (Fig. 4e). When the Cu pillar fractures and the crack-tip shielding effect is removed, the crack experiences overloading and grows rapidly in an unstable manner. It is noted that these results are only preliminary and further experiments are being conducted to understand the detailed mechanisms of crack interaction with these coarse grains. Nevertheless, the example is used to emphasize the ability to use this approach to address different problems in deformation of nanocrystalline structures.

In a broader context, the ability to fabricate and evaluate such specimens is also timely in that there is considerable worldwide research that is ongoing in the area of large-scale computations to model the deformation and fracture of multiphase materials with an important recognition for the need to link the underlying physical phenomena across length scales [8–12]. New methods are continually being evolved to accomplish this goal but are computationally expensive and prohibitive. Consequently, these methodologies have been restricted to two-dimensional calculations and/or idealization of microstructures, and relatively few examples exist that are three-dimensional and multiscale in scope [13]. In this regard, such spatially well-controlled microstructures

in thin film form that can be modified systematically and tested in situ provide an important function in that experimental results on them can serve to validate these new models that are being developed.

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