Grain-Size Growth Model Validated by *In Situ* Measurements of Nucleation and Growth

Using *in situ* heating transmission electron microscopy (TEM) methods, a team of researchers at Yale University has devised a technique to predict the microstructure resulting from crystallization. This ability allows researchers to tailor material properties that are sensitive to microstructure and is important to a broad range of fields that includes materials science, geology, physical chemistry, and biochemistry. There are theoretical models to predict the grain size and also experiments to monitor the growth of individual crystals. However, this research is the first to check the validity of theoretical predictions by comparing them to experimental observations that can separate the effects of nucleation and growth. These methods would enable researchers to predict grain size and the associated material properties that are dependent on microstructure.

In the September 19 issue of *Applied Physics Letters* (#124102; DOI: 10.1063/1.2053348), the Yale team of H.-J. Lee, H. Ni, D.T. Wu, and A.G. Ramirez reported a method of predicting grain size from the direct measurement of nucleation and growth rates. The researchers sputter-deposited amorphous 200-nm-thick equiatomic NiTi films onto silicon nitride TEM membrane samples, annealed them at various temperatures within a 200-kV field-emission TEM microscope, and took images during heating at 2-s intervals.

The researchers were able to monitor the crystallization events in real time. The amorphous NiTi films underwent polymorphic crystallization during annealing and transformation times that increased drastically from a few seconds to over an hour from the highest to the lowest temperatures. The researchers determined the nucleation rate and the growth rate by measuring the number of crystals and their size as a function of time. These results were compared with values derived from the conventional Johnson–Mehl–Avrami–Kolmogorov (JMAK) method of determining the area fraction and were found to be consistent. To verify their approach, the researchers compared the activation energies of nucleation and growth with the overall activation energy determined by the JMAK method and found these values to agree.

In contrast to the JMAK method, the novel contribution of this work is that the nucleation and growth rates are measured separately. This information allowed the researchers to use the mathematics of crystallization in a new way, namely, to deter-

Serpentine-Patterned Compliant Thin Films of Stiff Materials Reduce Strain During Stretching

Flexible electronic devices that can be stretched or bent have significant potential for numerous applications and are a major focus of current research activity. Most electronic materials, such as semiconductors, metals, and dielectrics, however, are stiff, and they fracture at small strains, typically under 1%. A possible way to create flexible electronics is to form thin films of these materials on an elastomeric substrate. However, the strains induced in these thin films would still be too large for various deformation modes, in particular, stretching. T. Li and Z. Suo, both from Harvard University, and S. Lacour and S. Wagner, from Princeton University, have now demonstrated that by patterning the thin film in the form of a serpentine on an elastomeric substrate, a large elongation may induce just a small strain in the film. Under appropriate conditions, the strain can be mitigated by out-of-plane twisting of the serpentine. Using finite element modeling, the researchers have shown that this principle can indeed be used for stretchable electronics.

In their article published in the December 2005 issue of the *Journal of Materials Research* (p. 3274; DOI: 10.1557/JMR.2005.0422), the researchers propose that a thin film of a stiff material can be patterned as a wide serpentine on a flat elastomeric substrate. This could serve as a platform on which electronic circuits can be fabricated using planar microfabrication technology. The finite element code ABAQUS was used to model and analyze the structure. The ratio of the Young's modulus of the substrate, E_{sub}, to that of the film, E_{film}, was assumed to range from 10^{-5} to 10^{-3}. For a relative elongation of 25%, the maximum strain in the film was shown to be <3.5% for a very compliant substrate with $E_{sub}/E_{film} = 10^{-5}$. On the other hand, for $E_{sub}/E_{film} = 10^{-3}$, the maximum strain was calculated to be 11.6%. Thus, the substrate needs to be sufficiently compliant for a smaller strain in the film. For a very compliant substrate, the maximum strain was also shown to be insensitive to the width and thickness of the serpentine, but was sensitive to the amplitude-to-period ratio. The larger the amplitude-to-period ratio of the serpentine, the smaller the strain levels in the film. In addition, the more compliant the substrate, the smaller were the maximum interfacial stresses.

The study showed that a thin film of a stiff material can be appropriately patterned on a sufficiently compliant substrate. Such a film would elongate by twisting out of plane so that large elongations of the substrate only induce small strains in the film (see Figure 1). The researchers said that such patterned films could serve as platforms on which entire electronic circuits could be fabricated. Such circuits are expected to function without appreciable fatigue, even when the substrate is subjected to repeated deformation. While only uniaxial elongation was considered in the study, the researchers said that the same principle can be extended to biaxial elongation.
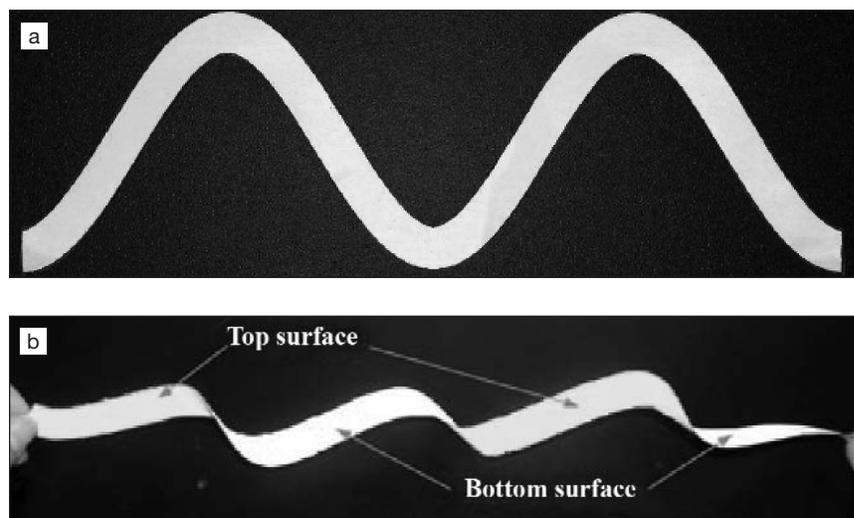
GOPAL RAO

Figure 1. (a) A piece of paper is cut into a serpentine. (b) When pulled, the serpentine elongates by twisting out of plane.

mine the average grain size after crystallization. This could not be done with conventional JMAK analysis because it gives an overall crystallization rate wherein the nucleation and growth rates are coupled. Armed with the ability to determine the rates of nucleation and growth independently, the researchers found them to be constant. By plugging these values into a mathematical expression from the JMAK theory, the researchers found that the experimentally measured grain sizes and the mathematical predictions agree over a broad range of temperatures. This method can be used in practical applications to control grain size and materials properties that are strongly related to microstructure.

TAO XU

Shock-Loading Strengthening Mechanism of Nanocrystalline Materials Revealed

The Hall–Petch effect, in which the strength or hardness of crystalline materials increases inversely with the square root of their grain size, makes clear that grain boundaries (GBs) are natural obstacles for dislocation motions. The limitations of the dislocation motion cause the increase in the hardness and strength of the crystal materials. When the grain size approaches the nanoscale, this strengthening mechanism is no longer applicable, because the grain boundary itself is susceptible to motion (e.g., sliding). Also, the dislocation tends to be unstable at such a small grain size. High-strain-rate deformation experiments, as in shock-loading conditions, have been found to exhibit increased strength in nanocrystalline Ni and Cu. However, the explanation of such a high strain rate (10^4 s^{-1} to 10^6 s^{-1}) is still not clear, since the high strain rate is increased in conjunction with increasing pressure. Now, a team of researchers led by Eduardo M. Bringa at Lawrence Livermore National Laboratory (LLNL) and Helena Van Swygenhoven at the Paul Scherer Institute (Switzerland) has used molecular dynamics (MD) simulations as well as experimental methods to verify the underlying strengthening mechanism at such shock-loading conditions in nanocrystalline materials.

As reported in the September 16 issue of *Science* (p. 1838; DOI: 10.1126/science.1116723), the researchers used MD simulations to systematically model shock-loading behaviors during the plastic deformation processes of Cu nanocrystalline materials at different grain sizes (5–50 nm) and shockwave pressures (5–47 GPa). The MD simulations showed that with increasing hydrostatic pressure, a nanocrystalline metal Cu that deforms plastically by GB accommodation (e.g., GB sliding) becomes harder, due to the reduction of the GB sliding and the initialization/emergence of dislocations along the GB. The researchers also performed high-resolution electron microscope (HREM) experiments on Ni nanocrystals after shock-loading at 40 GPa. Ni was used for the experiments because Ni and Cu are fcc materials with similar shock impedances, but Ni has a larger stacking fault energy. The dislocation activity is clearly seen by HREM inside the grains, in excellent agreement with the MD simulation results.

FENGTING XU

Bioelectronic Nanodevices Fabricated on Live Bacteria

Electrically percolating clusters of metal nanoparticles are ideal materials for electronic nanodevices because interparticle current occurs by single-electron transport. The negative surface charges of microorganisms such as viruses, yeasts, and bacteria, make them attractive scaffolds for templating metal nanoparticles. Now, researchers from the University of Nebraska–Lincoln have developed a method for building hybrid bioelectronic devices using gold nanoparticles and live bacteria. Furthermore, a biological response is used to control the electrical response of the devices.

As reported in an article published in the October 21 issue of *Angewandte Chemie, International Edition* (p. 6668; DOI: 10.1002/anie.200501711), V. Berry and R.F. Saraf deposited the gram-positive bacteria *Bacillus cereus* on a silica substrate containing linear gold electrodes 7 μm apart, 10 mm long, and coated with poly(L-lysine) (PLL). Filtration and ultracentrifugation were used to extract from culture similar-sized bacteria—about 4–6 μm in length and 0.8–1.0 μm in diameter. Typically, about 10 bridges formed along a pair of electrodes, which were 10 mm long, with a typical bridge composed of two bacteria. The researchers then immersed the bacteria-deposited chip in a solution containing PLL-coated gold nanoparticles (diameter = 30 nm). Berry and Saraf said that the deposition of the gold nanoparticles, regulated simply by time, is highly selective with formation of a gold monolayer only on the negatively charged bacterial surface, because both the nanoparticles and the substrate are positively charged. The negatively charged teichoic acid (a polyelectrolyte on the bacterium surface) wraps the particle, screening the particle–particle repulsion and making the monolayer electrically percolating. A standard assay showed that the bacteria survived the fabrication process.

The researchers actuated the hydrophilic bacterial cell membranes by controlling the humidity, thereby modulating the separation between gold nanoparticles and concomitantly the interparticle electron tunneling current. Defining a device as a single bacterial bridge and measuring normalized current as a function of relative humidity, the researchers found that a decrease in humidity from 20% to ~0% resulted in a >40-fold increase in tunneling current, even though the interparticle separation decreased by only 0.2 nm. Berry and Saraf said, "We believe that such hybrids will be the key to conceptually new electronic devices that can be integrated with live microorganisms on flexible, plastic-like substrates by using simple chemistry."

STEVEN TROHALAKI

Covalently Cross-linked Block Copolymer Micelles Encapsulate Magnetic Nanoparticles for Use in Biomedical Applications

Magnetic nanoparticles are currently used in numerous biomedical applications in which stability and surface functionality are crucially important. In the October 5 issue of *Nano Letters* (p. 1987; DOI: 10.1021/nl0513939), B.-S. Kim, J.-M. Qiu, J.-P. Wang, and T.A. Taton from the University of Minnesota reported the encapsulation of magnetic nanoparticles (γ-Fe$_2$O$_3$) within amphiphilic block copolymer micelles of poly(styrene$_{250}$-*block*-acrylic acid$_{13}$), which were subsequently cross-linked to secure the nanoparticles topologically. These "magnetomicelles" are stable to aggregation and have carboxylate groups on their surfaces that are readily modified.

The micelles, formed as a copolymer solution in *N,N*-dimethylformamide (DMF), were added to a second solution of nanoparticles in tetrahydrofuran (THF) in a defined ratio, forming a stable solution. Water was then slowly added to desolvate the copolymer core and nanoparticles simultaneously. Once cross-linked using a diamine cross-linker and a carbodiimide activator, the micelles offer a formidable defense against aggregation, changes in pH, and chemical etching from HCl (a known etchant of γ-Fe$_2$O$_3$ nanoparticles). No degradation of the nanoparticle cargo occurred during cross-linking. In addition, Kim and co-workers were able to alter the surface chemistry of the micelles by adding *N*-ethyl-*N'*-(3-dimethylaminopropyl)carbodiimide methiodide (EDC), N-hydroxylsulfosuccinimide sodium salt, and the fluorescent compound α-amino-γ-[5(6)carboxyamidofluorescein]-pentaethyleneglycol to the particle suspension. After this