Nano Focus

Ceramic nanomaterials that are light, strong, and spongy

Strong, ultralight materials could be used to make aircraft wings, battery electrodes, armor, and insulation. But today's high-strength low-density materials, such as silica and alumina aerogels, metal foams, and technical ceramics, are all brittle. They can crack or shatter when they are squashed too hard.

Julia Greer and her colleagues at the California Institute of Technology have now crafted nanoscale ceramic lattices that are strong and lightweight but also elastic. The materials spring back after being crushed down to more than 50% of their original height.

This work is part of a recent push to engineer strong, stiff, and lightweight materials by tailoring their structural design at the nanoscale. The theory is that in a conventional material, properties such as strength and density are correlated. However, those rules don't apply at the nanoscale. Researchers have used laser writing to carve complex, airy lattices of ceramics and metals. The tiny struts and trusses in these materials mean that the materials are mostly air and hence ultralight, but tough at the same time.

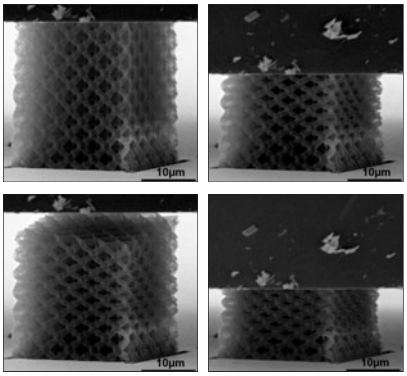
Greer and her colleagues make their nanoceramics using a technique called two-photon interference lithography. She used the method in 2011 to construct one of the lightest materials ever made: a microlattice of hollow metal tubes.

The researchers move a tightly focused laser beam in three dimensions across a viscous photo-reactive polymer. The polymer cross-links and hardens where the light focuses on it. The rest of the polymer is washed away, leaving behind a three-dimensional (3D) scaffold. Next, the researchers deposit a thin alumina film on the scaffold using atomic layer deposition. Finally, they use oxygen plasma to etch away the polymer inside the tubes, resulting in a 3D nanolattice made of a network of hollow ceramic tubes.

In this work, reported in the September 12 issue of *Science* (DOI: 10.1126/science.1255908; p. 1322), the researchers showed that the thickness of the hollow tube walls affects how the material deforms under compression. They made several lattices containing tubes that were 450–1380 nm in diameter and had wall thicknesses ranging from 5 nm to 60 nm. Then they compressed the different samples to see how they performed.

Lattices with thick-walled tubes—where the wall thickness was around 50 nm—failed catastrophically and shattered into fragments. Those with tubes that had thinner walls, about 10-nm thick, on the other hand, underwent a ductile deformation. The tube walls buckled locally but regained their original shape when the compression was removed.

"To date, no one has conducted such an in-depth study at the nanoscale with these exquisite structures," says Xiaoyu Zheng, an engineer at the Lawrence Livermore National Laboratory. "This work demonstrates that, through engineering of a material architecture and by control of feature sizes, intrinsically brittle materials can become ductile." Such lightweight, ductile, and strong nanostructured ceramic materials could open up a wide range of new applications, he says.



The sequence shows how the three-dimensional, ceramic nanolattices can recover after being compressed by more than 50%. Clockwise, from left to right, an alumina nanolattice before compression, during compression, fully compressed, and recovered following compression. Credit: Lucas Meza/Caltech.

The researchers currently make tiny cubes of the material that are 20 μm to a side. But, says Greer, her group is focusing on making larger volumes. She imagines making paper-like sheets of the material. "We could print such pieces of paper and laminate them together and we could then carve that into whatever shape we want."

But one drawback of two-photon lithography is that it is slow. "A 50 by 50 by 50 cubic micron piece made from alumina that's fully etched out takes about two hours," Greer says. Researchers might need to come up with a different technique to make the materials on a large scale, she says.

Prachi Patel

Blue phosphorescent OLEDs exhibit significantly increased lifetime

In a step that could lead to longer battery life in smartphones and lower power consumption for large-screen televisions, Stephen Forrest of the University of Michigan and his research team have extended the lifetime of blue organic light-emitting diodes (OLEDs) by a factor of 10.

Blue OLEDs are one of a trio of colors used in OLED displays such as smartphone screens and high-end TVs. The improvement means that the efficiencies of blue OLEDs in these devices could jump from about 5% to 20% or better in the near future, according to the researchers.

Phosphorescent OLEDs, also known as PHOLEDs, produce light through a mechanism that is four times more efficient than fluorescent OLEDs. Green and red PHOLEDs are already used in these new TVs—as well as in Samsung and LG smartphones—but the blues are fluorescent.

"Having a blue phosphorescent pixel is an important challenge, but they haven't lived long enough," said Forrest, the Paul G. Goebel Professor of Engineering.

Forrest's group, in collaboration with researchers at Universal Display Corp., have previously shown that, for blue PHOLEDs, a concentration of energy on one molecule can combine with that on

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a neighbor, such that the total energy is enough to break up one of the molecules. It is less of a problem in green- and red-emitting PHOLEDs because it takes lower energies to make these colors.

"That early work showed why the blue PHOLED lifetime is short, but it didn't provide a viable strategy for increasing the lifetime," said Yifan Zhang, a recent graduate from Forrest's group who is first author on a new study published in the September 24 issue of *Nature Communications* (DOI: 10.1038/ncomms6008). "We tried to use this understanding to design a new type of blue PHOLED," says Zhang.

The solution, which was demonstrated by Zhang and Jae Sang Lee, a current doctoral student in Forrest's group, spreads out the light-producing energy so that molecules are not as likely to experience the bad synergy that destroys them.

The blue PHOLED consisted of a thin film of light-emitting material sandwiched between two conductive layers—one for electrons and one for holes. Light is produced when electrons and holes meet on the light-emitting molecules.

If the light-emitting molecules are evenly distributed, the energetic electron–hole pairs tend to accumulate near the layer that conducts electrons, causing damaging energy transfers. Instead, the team arranged the molecules so that they were concentrated near the hole-conducting layer and sparser toward the electron conductor. This drew electrons further into the material, spreading out the energy.

The new distribution alone extended the lifetime of the blue PHOLED by three times. Then, the team split their design into two layers, halving the concentration of light-emitting molecules in each layer. This configuration increased the lifetime tenfold.

Nano Focus

Gradient microstructures alleviate pitfalls of nano-grained metals

While steel may be the benchmark for high-strength metals, materials science and engineering is now able to engineer materials that surpass this standard. Through processes such as grain refinement, metals that are typically thought of as much weaker take on unprecedented properties that rival those of traditional and even high-strength steels. This process of grain refinement strengthens metallic materials by reducing the average grain size to the nanoscale. While this may improve the strength of the material it is not without its drawbacks. Metals that are often very weak and ductile such as copper or aluminum experience a significant increase in strength when processed to have nanosized grains. However, they often become very brittle, which leads to cracking and premature failure. The origin of this brittleness, which is seen in tension, is attributed to localized strains occurring at the grain boundaries. This localization of strain in the nano-grains results in void formation and intergranular cracking.

One solution to this problem of tensile brittleness has been reported by K. Lu of Shenyang National Laboratory for Materials Science in Shenyang, China, in the September 19 issue of *Science* (DOI: 10.1126/science.1255940; p. 1455). Lu studied gradient microstructures in copper to resolve the problem of increased tensile brittleness that accompanies nano-grained metals. Gradient microstructures are categorized by a gradual increase in grain size, starting from nanoscale grains at the surface to a more coarse-grained microstructure near the center. The researchers were able to induce this unique type of microstructure by generating a strain gradient in a coarse-grained metal so as to cause increased deformation near the surface.

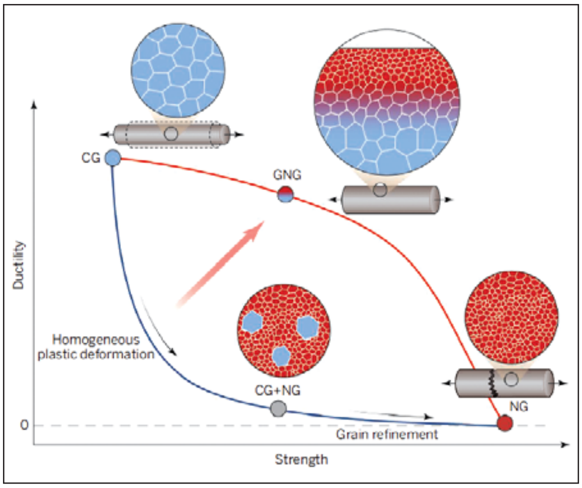

Illustration of the tradeoff between strength and ductility that typically accompanies the shift from a coarse-grained (CG) to nano-grained (NG) microstructure (lower curve). This is compared to the synergy achieved with gradient nano-grained (GNG) structures (upper curve). Credit: K. Lu.

This novel approach to microstructural engineering also leads to the enhancement of other mechanical properties. Microstructural plastic deformation under tension, which typically occurs prior to failure in these materials, occurs simultaneously throughout materials with a very narrow grain-size distribution. In materials with a grain-size gradient in contrast, plastic deformation begins first in the coarse-grained region before transmitting into areas of finer and finer grains as the applied load is increased. This gradient effect helps to relieve strain localization, which leads to an increased yield strength (the onset of irreversible deformation) without sacrificing ductility. The researchers also found that this exterior gradient of finer grains helps to improve fatigue resistance and suppress detrimental surface cracking. This work has helped to explore gradient grained materials that retain the ductility of metals with coarse microstructures, while still benefiting from the enhanced strength of nanoscale grains.

Ian J. McDonald