

Fe-Based Amorphous Alloy Rods with 12-mm Diameter Developed

Amorphous Fe-based alloys show several properties that are superior to those of their crystalline counterparts and structural steels. They have higher strength and hardness, superior corrosion resistance, and better magnetic properties, depending on the application. However, because of their limited glass-forming ability, until now it has only been possible to form rods with maximum dimensions in the range of 4 mm. If these alloys are to be used for structural applications, it is necessary to form much larger blocks of the material. It was recently shown that the addition of yttrium improves the glass-formability of Fe-based alloys. The larger Y atoms induce atomic-level stress that was shown to retard crystal phase formation, with the system left in a vitrified state on cooling from the melt.

Two new studies have now used this principle to develop structural amorphous Fe alloys with maximum thickness diameters approaching 12 mm. V. Ponnambalam, S.J. Poon, and G.J. Shiflet of the University of Virginia reported the development of Fe-based bulk metallic glasses with thicknesses of more than 1 cm by alloying Y and Er in the May 2004 issue of the *Journal of Materials Research* (p. 1320). Z.P. Lu, C.T. Liu, J.R. Thompson, and W.D. Porter of Oak Ridge National Laboratory reported their work on developing amorphous Fe alloy rods with large diameters in the June 18, 2004, issue of *Physical Review Letters* (245503). The two studies go a long way in forging a path toward the ultimate goal of using amorphous Fe-based alloys for structural applications.

Poon and colleagues used an Fe-Cr-Mo-C-B alloy system with 2% yttrium and erbium, a lanthanide, in the alloy (see Figure 1). The Y/Er-to-Fe atomic size ratio is about 1.4, which is close to the largest practically attainable value in Fe-based alloys. Samples were prepared by injecting the molten alloy into a copper mold under optimized casting conditions. Rods of up to 12 mm in diameter were found to remain amorphous, as confirmed by x-ray diffraction (XRD). The Young's modulus of the material was ~200 GPa, with the bulk modulus in the range of 180 GPa. Tensile strength, based on microhardness measurements, was ~4 GPa, with hardness values of ~13 GPa. The research team hypothesized that the metastable Fe₂₃C₆ phase that forms upon devitrification of Fe-Cr-Mo-C-B becomes less stable when alloyed with Y and Er. Lanthanide elements other than Er, such as Dy, Yb, and Gd, also yielded similar amorphous Fe alloys.

For their investigations, Lu and col-

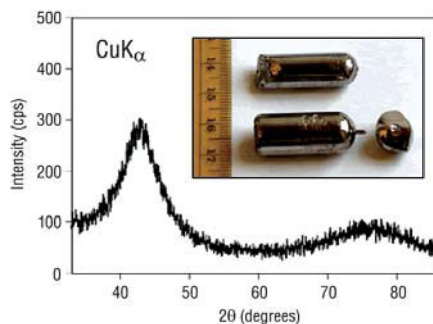


Figure 1. X-ray diffraction pattern for an Fe-Cr-Mo-Er-C-B sample, revealing its amorphous nature. The inset shows a photo of (top) 10-mm-diameter and (bottom) 12-mm-diameter glassy rods as well as a small segment obtained from a 12-mm-diameter glassy rod. Reproduced with permission from the *Journal of Materials Research*.

leagues used a Fe-Cr-Co-Mo-Mn-C-B system with 1.5% Y added. Alloy ingots were obtained by arc-melting a mixture of the metals and elements, which were then remelted and drop-cast into a copper mold. XRD and optical microscopy were used to confirm that the material was amorphous. It was shown that 12-mm-diameter rods could be obtained for a certain compositional range in a pseudo-ternary phase diagram. When cast without Y, the material immediately showed crystalline characteristics. The Young's modulus of the new amorphous material was more than double that of bulk amorphous Pd-Cu-Ni-P metallic glass, and nanoindentation hardness values were more than triple. The materials were paramagnetic at room temperature and became ferromagnetic at cryogenic temperatures. The research team hypothesized that the superior glass-forming ability of the new alloys is due to lower eutectic temperatures and a shift of the composition to the eutectic, wherein glass formation is thermodynamically favored. Also, addition of Y retarded the nucleation and growth of Fe carbides, the primary phase, on cooling from the melt. The yttrium addition destabilized competing crystalline phases while stabilizing liquid phases.

Both studies have demonstrated that the addition of a minor alloying element is extremely effective in promoting bulk metallic glass formation in Fe alloys. These studies suggest that in the future such materials could potentially replace conventional high-strength steels in structural and other applications. In a separate study, William L. Johnson and colleagues at the California Institute of

Technology reported in the June 18 issue of *Physical Review Letters* (245504) that the addition of Y to a Cu-Zr-Al system was also shown to yield the formation of amorphous copper alloys with dimensions of up to 12 mm.

GOPAL RAO

Conductance in Single DNA Molecules Directly Measured

The direct measurement of conductance in single DNA molecules is important for the study of charge transport, which is important in human health issues, and biosensor applications. Although DNA conductance measurements made in recent years show characteristics varying from insulator to superconductor, several requirements for reliable measurements have been made clear: that electronic coupling between DNA molecules and electrodes be reproducible; that a signature is discovered that identifies the conductance with a single DNA molecule; and that the measurement be performed in an aqueous buffer in order to preserve the native conformation of the DNA. N.J. Tao and co-workers at Arizona State University have met these requirements and have directly measured the conductance of single DNA molecules (with varying length and sequence) covalently bonded to electrodes in aqueous solution.

As reported in the June 9 issue of *Nano Letters* (p. 1105), the researchers measured the conductance of two series of DNA sequences: (GC)_n, where n = 4–7; and CGCG(AT)_mCGCG, where m = 0,1,2. Both series are self-complementary and spontaneously form stable B-form helices in solution, which is typical of most native DNA. Both DNA series are capped at each end with -CH₂CH₂CH₂SH groups. The researchers formed molecular junctions between a Au electrode and a Au tip of a scanning tunneling microscope (STM) that was insulated over most of its area to eliminate unwanted current leaks. In a buffer solution containing 3 μM DNA, the STM tip was repeatedly moved into and out of contact with the electrode. Once the STM tip made contact with the electrode, a piezoelectric transducer was activated and pulled the electrode out of contact with the tip. DNA molecules then bridged the gap between the STM tip and the electrode.

Molecular junction formation results in a series of steps in a plot of conductance as a function of tip-electrode separation. For (GC)₄, the steps are approximately multiples of a fundamental conductance, 1.3 × 10⁻³G₀ (where G₀ = 2e²/h ≈ 77 μS, which is on the order of the conductance of a single gold atom connecting the two electrodes). The researchers attributed each step in the

conductance to an additional DNA molecule forming a junction. They said, however, that conductance steps do not always

have the same values, which reflect microscopic differences in the DNA–electrode contacts. The researchers therefore took

Diatom Frustules Serve as Scaffolds for 3D Polymeric Structures with Nanoscale Features

Shape-tailored microscale polymeric structures with feature sizes down to the nanoscale are becoming increasingly important for various applications, such as in microelectromechanical systems. Current techniques, such as lithographic-based layer-by-layer fabrication, are not well suited for the production of three-dimensional polymeric structures with complex shapes. In addition, large numbers of polymeric structures with a specific shape need to be created. C. Gaddis and K. Sandhage of the Georgia Institute of Technology have now demonstrated a technique that uses diatoms—single-celled algae—as scaffolds to form free-standing microscale polymeric structures. Diatoms have amorphous silica nanoparticle-based rigid cell walls (frustules). In this study, a thin (submicron) polymeric coating was applied to diatom frustules. The underlying silica frustules were then dissolved, leaving behind the polymer with the shape and features of the diatoms.

Diatom frustules come in a wide range of shapes with nanoscale features. They can be precisely replicated in a massively parallel manner with ease. The frustules used in this study, as reported in the *Journal of Materials Research* (Web release date of accepted preprint, July 1) had hollow cylindrical shapes with diameters of 8–12 μm and mesoscale pores with diameters of several hundred nanometers in rows along the cylinder length. After being cleaned, the diatom frustules were dipped in a coating solution containing a two-part, 5-min-curing epoxy mixture dissolved in acetone. After evaporation of the acetone, the epoxy was allowed to cure. The concentration of the epoxy in the solution

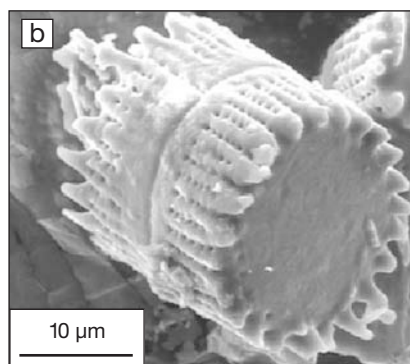
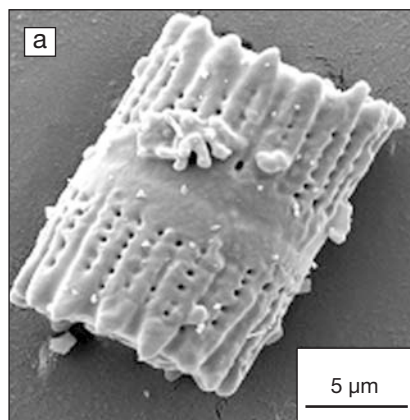


Figure 1. (a) Secondary electron image of a silica-based diatom frustule used as a transient scaffold; (b) secondary electron image of an epoxy structure derived from a diatom frustule scaffold. Reproduced with permission from the *Journal of Materials Research*.

was adjusted to obtain a coating that preserved the pores and fine features of the diatom frustules. The coated frustules were then dipped in hydrofluoric acid to dissolve the silica diatom shells, leaving behind the polymer coatings in the shape of the diatoms (see Figure 1). Gaddis and Sandhage found the polymer structures to be very similar in morphology to the starting diatom frustules.

In addition to diatom species, other self-replicating biomineralized micro- and nanostructures (such as microshells and sponges) can be used to yield various 3D polymeric shapes with desired morphologies. The technique is not limited to naturally available diatoms or biomineralizing organisms. According to the researchers, genetic engineering could be used in the future to produce replicable bioscaffolds with non-natural shapes. The polymeric coatings are not confined to epoxy-based compositions. Other polymer structures can be produced, so long as a dilute coatable solution can be formed and the underlying scaffold can be removed, leaving the polymer structure intact without being affected by the selective dissolution treatment. Upon scaleup, the researchers said, the current process can be used to produce large quantities of inexpensive three-dimensional polymer micro/nanoscale structures for use in various biomedical, chemical, catalytic, photonic, aerospace, and other applications.

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more than 500 measurements and constructed a conductance histogram in which they found peaks that occur at multiples of $1.3 \times 10^{-3}G_0$. Conductance histograms of other DNA duplexes also displayed peaks, but at multiples of different values. For $(GC)_n$, the researchers found that the conductance is a linear function of reciprocal DNA duplex length, measured in base pairs. The conductance of the CGCG(AT) $_m$ CGCG duplexes does not decrease nearly as slowly with length as the conductance of the (GC) duplexes and can be fit by a function of the form $A \exp(-\beta L)$, where A ($1.3 \times 10^{-3}G_0$) and β ($0.43 \pm 0.01 \text{ \AA}$) are constants and L is the length of the AT segment.

The researchers said that their findings are consistent with previously published models that describe charge transport in DNA as a tunneling-like process for short DNA and a hopping-like process for relatively long DNA duplexes.

Tao said, “The sensitive dependence of the conductance on the DNA sequence suggests the possibility of reading the chemical information of DNA via direct conductance measurement.”

STEVEN TROHALAKI

C₆₀-Based Organic Diode Performance More than 100× Better than Other Organic Semiconductor Devices

In recent years, organic semiconductor devices (OSDs) have found increasing practical applications in displays, transistors, lasers, memory, and diodes. So far, however, their performance has lagged far behind their inorganic counterparts, particularly with respect to response speed and current density. L.P. Ma, J.Y. Ouyang, and Y. Yang of the University of California, Los Angeles, have achieved a more than 100-fold improvement in response speed and current density, compared with common OSDs, with their C₆₀-based organic diode, formed with one ohmic contact and one rectifying contact. As reported in the June 7 issue of *Applied Physics Letters* (p. 4786), the researchers used a C₆₀ electron acceptor layer sandwiched between a Cu cathode and an Al anode; they heat-treated the device for 5 min at 120°C to achieve the huge leap in performance.

The scientists fabricated the organic diodes by first depositing Cu using thermal vacuum deposition onto a smooth glass substrate followed by C₆₀ (100 nm thick) and Al, creating a 0.0625 mm² device. Only after the heat treatment did the scientists measure injection current densities of 363 A/cm² at 2.4 V and 1 MHz current responses. Previous attempts to