Defects and plasticity account for ultrastrong properties of supercrystalline nanocomposites

Nanotechnology is leading to widespread development of new devices such as wearable sensors, catalysts, and batteries. In many of these applications, nanoparticles are embedded in a matrix to form nanocomposites. These composites must not only be multifunctional but also structurally sound, to withstand processing steps that take them from the nano- to macroscale, and strong and resilient enough mechanically while in service.

Recent work at the Hamburg University of Technology, in collaboration with the University of California, Berkeley, and the Institute of Materials Research in Geesthacht, Germany, has focused on the deformation mechanisms and the role of defects as a way to understand the strength of nanocomposites. As reported in *Science Advances* (<https://doi.org/10.1126/sciadv.abb6063>), the researchers focused on a subcategory of nanocomposites called supercrystalline nanocomposites, in which nanoparticles surface-functionalized with organic ligands are assembled in a periodic lattice, similar to atoms in a crystal.

The supercrystalline nanocomposites in this work consisted of spherical iron oxide (Fe_3O_4) nanoparticles, an earth-abundant material, functionalized with oleic acid. After their self-assembly into a so-called superlattice, heat treatment

at mild temperatures ($<325^\circ\text{C}$) induced cross-linking of the organic ligands, and in turn the material's strengthening.

The resulting superlattice is face-centered cubic (fcc) with a lattice parameter of 24.5 nm and interparticle spacing of 1.5 nm. The researchers studied structural features via electron microscopy and mechanical behavior under nanoindentation, correlating the two. They verified that the organic ligands' cross-linking is a powerful strengthening mechanism, leading to the replacement of van der Waals interactions by stronger covalent bonds in the organic network surrounding the Fe_3O_4 nanoparticles. The nanocomposites became, therefore, extremely strong and stiff with bending strength of 630 MPa, elastic modulus of 60 GPa, and hardness of up to 4.7 GPa, values similar to conventional alloys and ceramics. At the same time the supercrystalline nanocomposites provided a useful fracture toughness of $\sim 0.5 \text{ MPa}\cdot\text{m}^{1/2}$ after cross-linking. The mechanical properties obtained are among the highest achievable in supercrystalline nanocomposites consisting of $\sim 16\text{-nm}$ spherical nanoparticles functionalized with an ultrathin layer of oleic acid.

This kind of material can be further tuned to feature superparamagnetic behavior in bulk form. This rare effect can be achieved thanks to the ultrarapid heating that techniques such as spark plasma sintering offer, allowing excellent control of the material's nanostructure. Here, sintering leads to the formation of necks between the nanoparticles (each a nanocrystal), which

in turn retain a size below 20 nm. This fine-tuned nanostructure guarantees mechanical integrity while preventing the magnetic interactions that lead to loss of superparamagnetism in bulk materials. As reported previously in *Nanoscale Advances* (<https://doi.org/10.1039/C9NA00222G>), the nanocomposites achieved a high magnetic moment and magnetic permeability but low coercivity. This combination of properties is ideal for applications when frequent magnetic switching is necessary and heat-associated material degradation needs to be prevented, such as high magnetic response substrates and transformer cores in energy applications.

The elastoplastic behavior of the supercrystalline nanocomposites is explained in this work in terms of classical shear theories of crystalline materials. They form material defects such as dislocations, twins, and small-angle grain boundaries when exposed to mechanical deformation very much like alloys. This is understandable in fcc structures, but looking at the energy barriers for defects, it is surprising. The line energy for dislocations scales with the square of their Burgers vector, leading to 1000 times higher energy for dislocations in this superlattice compared to metals.

"The ability to endure deformation by classical crystal defects combined with the ability to compact under load makes the supercrystalline nanocomposites promising candidates for applications where functionality and structural integrity are required," says Gerhard Dehm, director at the Max Planck Institute in Düsseldorf, who leads a research team on Structure and Nano-/Micromechanics of Materials. "Changing cross-linking between the nanoparticles, their size and size distribution opens routes to tailor the mechanical properties and the work of Giuntini, Schneider et al. has laid the foundation for this." Dehm was not involved in the present study.

According to Diletta Giuntini, the lead author of these studies, these are not only fundamentally interesting

Sub-indent deformation mechanisms in cross-linking-strengthened supercrystalline nanocomposites, showing plastic deformation and compaction. Credit: *Science Advances*.

insights on the analogies between crystals and supercrystals, but they also pave the way toward fine-tuning the mechanical behavior of supercrystalline nanocomposites. Scientists

will ultimately be able to strengthen the materials chosen for their functional properties, but also to engineer structural materials—that is, ceramic-organic nanocomposites with

outstanding combinations of strength and toughness—while retaining the nanoparticle properties up to the macroscales.

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